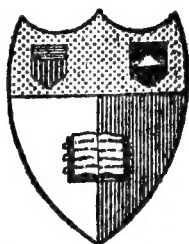


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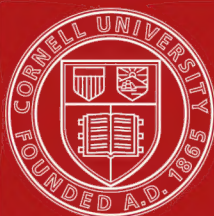
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ESTATE RUBBER

ITS PREPARATION, PROPERTIES AND TESTING

BY

Dr. O. DE VRIES,

DIRECTOR OF THE CENTRAL RUBBERSTATION
BUITENZORG (JAVĀ).



BATAVIA
DRUKKERIJEN RUYGROK & Co.
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PREFACE.

This book is a translation and extension of a treatise which appeared in Dutch in the beginning of 1919. The original Dutch edition was principally destined for the use of planters and of those directly interested in the plantation rubber industry. We have thought it worth while to furnish the English edition with more figures and technical details which may be of interest to the rubber chemist, and to include the principal data from the already rather extensive literature on plantation-rubber. In order to give the reader an idea of the present state of our knowledge on each subject we have added in small type reviews of the rather scattered and sometimes little known original sources from which we quoted. We have taken care only to cite such papers as we could consult ourselves, so as to avoid the errors in quotation and the incorrect conclusions still too common even in some of the best known textbooks. Completeness, of course, is almost unattainable in such work; still we have striven to bring the literature on each point together as fully as possible.

The author had the privilege of writing under the stimulus of close contact with the plantation end of the industry, and of the mass of experimental material gathered at the research and testing laboratory of the Central Rubber Station at Buitenzorg. In giving a review of the present state of our knowledge on the preparation and properties of plantation rubber we hope to awaken the interest of the producer as well as of the consumer of rubber. Convinced as we are that real, sound knowledge is the best basis for an important industry in which both the preparation and the manufacture are so much in need of adequate technical supervision, it is our hope that this book may further the development of the

rubber industry and in some measure do away with the suspicions and prejudices which still hamper the handling of this increasingly important staple product.

Our warm thanks are due to Dr. C. D. LA RUE, then botanist to the General Rubber Co at Kisaran (Sumatra) and to Mrs. LA RUE, who with true scientific enthusiasm undertook the task of translating the original Dutch edition into English, and who redressed our linguistic shortcomings in part of the enlarged manuscript; and to WYKEHAM PRICE of Batavia, who greatly helped us by looking through the greater part of the manuscript.

Buitenzorg, July 1920.

The Author.

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INTRODUCTION.

The time is not yet long distant since ideas on the properties of rubber and on the objects to be attained in rubber preparation were quite vague and confused. An exaggerated anxiety on rather unimportant points was as often found as astonishing carelessness in matters of prime importance. Manufacturers complained but did not formulate their complaints in such a way as to make planters readily understand what they wished. On the market, and often also amongst planters, great importance was attached to minor points whilst fundamental questions did not draw the attention they deserved. As examples one need only mention the great pains taken to use non but red glass or red curtains to subdue the light in the drying sheds, or to recall the energy displayed in neatly trimming and cutting the edges of the crepe, whilst no thought was given to mixing and bulking the latex or to the standardisation of methods of preparation in general.

Thanks to the investigations made by several institutes, in Europe as well as in the Tropics, our knowledge of rubber and its preparation has greatly increased in recent years; and though many questions still remain unsolved, especially regarding the manner of expressing different properties and the value attached to them by manufacturers, our insight into many points has become so much deeper that it seems worth while to give a review of the present status of our knowledge. Doubtless, as research work proceeds, present opinions will have to be altered on many points; and in treating different questions we shall often have to record a „still unknown“ in this book. But the fact that many points are yet to be cleared up, does not diminish the desirability of making known in wider circles what knowledge has been gained already.

In treating the preparation of plantation rubber, we shall restrict ourselves to those points that are of importance in connection with the properties of the product. Other points as, for instance, the utensils used, the control of the work, and a number of practical trifles which are of eminent importance for the estate staff, will remain wholly untreated here, because nothing is known or can be said about their relation to the properties of the rubber. The practical man may be referred to the excellent handbooks in which these subjects are treated with special regard to the local circumstances determining them.

The science of rubber and rubber-testing is still in its infancy; broad principles have only here and there been worked out. The eventual relations between the different properties, which are determined in ordinary testing, are only partly known; the relations between these properties and the practical results obtained in rubber-manufacture have in many respects still to be determined. A statement that a certain rubber is, or is not, fit for a certain manufacturing purpose must often be based on a sort of guess instead of on a real test; in many cases the rubber has to be tested in the form of the finished article, if one wishes to know how its exact behaviour will be. Whilst, therefore, the testing of rubber for the practical purposes which the manufacturer has in view, is still very incompletely worked out, the lines along which we had to start our testing-work were easier to draw. Our aim must in the first place be to make plantation-rubber as good and as uniform as possible. In endeavouring to do this, some of the principal properties can first be selected to work upon; as the work proceeds, and the wishes of the buyers become more pronounced, other points can also be taken into consideration.

In judging the inner properties of rubber we have taken the standpoint that rubber is becoming more and more a mass-article, so that, for the principal types, „good and uniform” is the first thing to strive after. Whether a demand for special types will gradually develop is as yet uncertain. It may be safely stated that fancy-grades in general do not find adequate appreciation and that types differing from

the normal ones are regarded with suspicion rather than welcomed enthusiastically. The efforts to produce a type with special properties which would fetch a higher price on the market have as yet not met with success, and for the greater proportion of plantation-rubber the tendency is toward a few well known forms of as good and uniform properties as possible.

In our investigations and testing work we have expressed the properties of the rubber by a method which gives, in our eyes, a more exact and complete idea of them than is found in many publications for the same purpose; but we do not doubt that there are still a number of properties, which incidentally may be of great importance to manufacturers, but which are not taken into account in our testing.

Rubber is a colloid and shows the complicated properties of this class to the highest degree; and it is used for so many purposes that quite a number of independent properties would have to be determined to enable one to judge of its value in all exigencies to which it may be put. Moreover, research work on rubber testing in which the way should be indicated by workers from the manufacturing side is still much too scarce, or at least much too seldom published and made available for general use.

The method by which tensile strength, rate of cure, slope, and viscosity are determined in our testing work, and the significance of these properties in judging the rubber, will be extensively treated in Chapters XVII-XIX. Here we only wish to emphasize that quality strictly, speaking, is expressed by tensile strength and slope (resistance to stretching at high elongations); a high tensile strength and a small figure for slope indicate a rubber of good quality, whilst the lower grades may deviate markedly in this respect.

Besides quality in a mass-article as rubber one also desires uniformity; and in the first grades besides tensile strength and slope which are in most cases good and sufficiently uniform, it is principally the rate of cure that gives rise to complaints on lack of uniformity. It is certainly true that a deviation in rate of cure is not irreparable; it can be remedied by properly choosing

the mixture (eventually by using artificial accelerators), and by adjusting the time of cure — quite different therefore from a deficiency in tensile strength or slope which cannot be repaired. The opinion of some investigators, who regard every increase in rate of cure of the raw rubber as an advantage and judge the rubber principally on its rate of cure, is in our eyes beside the mark. It will be of little importance to manufacturers whether the bulk of smoked sheet or fine pale crepe vulcanises in a 5 minutes shorter or longer time, but it is most emphatically desired that different lots, and different pieces from one lot, show as much as possible the same time of cure. Every marked deviation from the general average is troublesome, and especially undesirable in a mass-article; the greatest care should be taken in so choosing methods of preparation that the first grade product shows standard properties and a high grade of uniformity in respect to rate of cure.

Besides the above named principal properties for a product destined largely to be vulcanised, we use in testing some auxiliary ones foremost of which is the viscosity in dilute solution. On the properties after vulcanisation and the uniformity in vulcanizing capacity, viscosity determinations do not allow of direct conclusions; but as the viscosity is very sensitive to all kinds of influences in preparation it is very valuable in our kind of work, when combined with the above named vulcanisation testing. It often clearly indicates, where the cause of a certain deviation or shortcoming is to be looked for.

A determination of chemical composition also may give indications in many cases, although this varies in Hevea-rubber only within small limits and has not the same importance as the analytical data on rubber of other botanical origin.

To control and improve the properties of rubber, one has to consider which factors in culture and preparation give the rubber its good or bad properties. In reviewing the data on these points, we shall see that the *tensile strength* in the first grade product is usually satisfactory but that there are some factors which cause a lower

tensile strength than normal. It is not yet known how this may be avoided. Taking young plots into the tapping round is one of the factors which may often cause a deficiency in tensile strength of the product of an estate; unfavourable outside circumstances, such as prolonged drought, may be another. One may suppose that in such cases the trees produce a caoutchouc-hydrocarbon of inferior properties but the proof of this assertion is yet lacking.

For the rest, tensile strength is not influenced by the usual variations in methods of preparation; also those cases which are generally suspected as very harmful, such as strong dilution of latex which gives a weak coagulum, or prolonged heavy crepeing which is supposed to destroy the „nerve” or „fibre,” do not cause a deterioration in tensile strength. It is only by really destructive processes, as oxydation, tackiness, decomposition by overheating, etc., where the caoutchouc-hydrocarbon itself is attacked, that the tensile strength is markedly decreased.

The *slope*, also, is not affected by most of the factors in ordinary preparation. A clear insight as to the factors which give an increase in slope and, therefore, a weaker, less resistant, rubber has not been obtained; it is evident, however, that in some way the caoutchouc-hydrocarbon itself comes into play and that a small figure for slope means a pure and superior rubber.

For the *rate of cure* of plantation rubber its content of non-rubber substances, viz. the serum constituents and their decomposition-products, is principally responsible. These substances act as catalysts in accelerating or retarding the cure. The rate of cure is, therefore, most fundamentally different from the tensile strength and slope which constitute properties of the colloidal caoutchouc-hydrocarbon, whilst rate of cure is dependent upon the admixtures or „impurities”. Amongst these, one has to think not only of those constituents that are already present in the latex and which the rubber absorbs during coagulation, but also of the decomposition-products that may be formed from these constituents in the course of preparation. Further, the

chemicals added during preparation may play a role and that again in two ways: firstly on their own account acting as chemicals or catalysts and secondly, by changing the non-rubber substances or influencing their decomposition. A fourth group of non-rubber constituents is formed by the foreign products that are absorbed by the rubber during the smoking process.

The large number of substances which fall under these four heads is the cause that nearly every change in the method of preparation produces a deviation in rate of cure. As long as these deviations are small they are of no great practical importance as small differences in rate of cure, for instance between the product of different estates, are in all cases to be expected. In certain circumstances, however, the deviations may become very large. For instance, maturation may give a very rapid curing rubber and many smaller, but not unimportant, deviations in rate of cure are to be explained by a beginning of maturation. On the other hand, some chemicals, such as formalin and alum, may retard the rate of cure very markedly.

It would be false, however, to suppose that differences in the method of preparation are the only or the principal cause of variability in rate of cure, and that standardising methods of preparation will suffice to obtain a uniform rubber from all estates. Differences in composition of the latex itself cause as large variations in rate of cure as any other factor; and the more the methods of preparation become standardised, the more important this group of factors will become as a cause of variability, because the age of the trees, the tapping, and the general physiological conditions are factors that cannot be altered or standardised at will. Very large deviations in rate of cure may be due to causes under this head; amongst them may be mentioned the tapping of trees after a period of rest when an abnormally slow curing rubber is obtained.

As stated above, the *viscosity* in dilute solution is very sensitive to all kinds of influences. A decrease in tensile strength seems to be always accompanied by a decrease in viscosity, at least as long as it is not caused by such factors

as particles of dirt etc. The catalysts which increase or decrease the rate of cure have an influence on the viscosity also; in many cases an increase in rate of cure is accompanied by an increase in viscosity, but in quite a number of other cases an increase in rate of cure is coupled with a decrease in viscosity. Furthermore, some factors (such as gentle heating) cause a decrease in viscosity while leaving the properties after vulcanisation unchanged. The viscosity, therefore, seldom allows a definite conclusion as to the properties after vulcanisation, but is of much value when determined in addition to these.

Of special interest are determinations on the effect of ageing of rubber, of the raw product as well as of the vulcanisate. A colloid as rubber is not stable, but changes in properties and has its complicated history, influenced by all factors which acted upon it in earlier stages. The vulcanised product is far less stable than the raw rubber; but, as far as our present knowledge goes, neither the properties of the latex nor the usual variations in the methods of preparation are of much importance on the ageing properties. Only very peculiar methods of preparation may cause the raw product to deteriorate more rapidly than usual, whilst the changes in vulcanised rubber seem to be due more to the mixture and the method of vulcanisation than to the rubber itself; and many disappointments caused by deterioration of vulcanised articles have probably quite unjustly been brought to the charge of plantation-rubber, instead of being ascribed to manufacturing processes. A careful and detailed investigation of the ageing properties, however, certainly deserves full attention and it is to be hoped that methods will soon be worked out which will give quick and easy tests on this point.

Finally there are many properties of raw rubber which may be of importance in the manufacturing processes but for which adequate methods of determination have not yet been worked out; these, therefore, have not received the attention they deserve. We think, for instance, of the plasticity of the raw product, the ease with which it breaks

down on hot rolls and takes up chemicals and compounding ingredients, the rate with which it dissolves in the usual solvents, and the properties of such solutions after different treatments of the raw product. Even such properties as the tendency of different sheets to stick together in the chests are by no means sufficiently studied and explained so that much work remains to be done on such points where a cooperation between workers from the manufacturing and the planting side might be very fruitful. One of the aims in writing this book has been to stimulate such a cooperation which will be best furthered by treating the subject in the broad ways of general science, i.e. by free and open discussion.

Besides the inner properties, which will be given the prominent place they deserve, the exterior ones will not be neglected in treating the properties and preparation of plantation-rubber because they play such a role on the market and, to a great extent, determine the saleability of the product. Shortcomings in external appearance immediately awaken a strong distrust and the suspicion that the preparation may have been deficient. Besides an adequate care for the inner properties and uniformity of the product, great attention has to be paid to its outer looks.

The claims on the quality and appearance of the rubber have further to be weighed against the practicability and the costs of different methods of preparation. Further, the prescriptions have to be chosen so that in ordinary estate practice, with the labour-force and supervision at ones disposal, the desired product of good and uniform properties is in all circumstances obtained.

We shall now, with these questions before us, treat systematically the preparation of plantation-rubber in all its phases, from the latex to the finished product. It will be seen that even the latex, as the trees produce it, causes many differences in properties of the rubber. In further preparation there are many factors that have a large influence on the properties of the rubber; but there are others that are without importance in this respect, and

upon which economy or practical considerations alone must decide. Summarising the data so obtained, we shall try to indicate the methods that, according to the present state of our knowledge, are to be most strongly recommended in order to obtain as good, as uniform, and as cheap a product as possible.

CHAPTER I.

THE L A T E X.

§ 1. Description.

Latex is a milky fluid, which on microscopic examination is found to consist of numerous minute rubber globules suspended in a watery liquid. The rubber globules are constantly vibrating, showing the so-called Brownian movement; their diameter varies from 0.0005 to 0.003 mm.

The number of these small particles in a given volume of latex is, of course, enormous; 1 cc. may contain 50000 millions, or one gallon of ordinary latex more than 200 billion globules.

See f.i. V. HENRI, C.R. 144 (1907), 432; C.Gp. 1907, 511; Lectures 1908, 203.

The globules in latex from the leaves and young twigs are smaller than in latex from the stem; and in young trees they are smaller than in older trees.

Ph. SCHIDROWITZ (Rubber (1911), 117) found globules of about 0.0005 mm in a very young plant, whilst in older trees the latex showed globules of 0.001 to 0.002 mm.. Similar observations were made by T. PETCH (Phys. & Diseases (1911), 18), who also mentioned globules with a tail.

W. BOBILIOFF (Arch. 3 (1919), 374 and 405) has made an extensive study of this subject; he distinguishes different types of rubber globules: very small round globules, in diameter smaller than 0.0005 mm.; round globules up to 0.002 mm.; pear-shaped globules, 0.0015—0.002 mm.; and pear-shaped globules with a tail, 0.0015—0.003 mm.. He describes their occurrence in different parts of the tree, and finds that leaves and young twigs contain very small globules, whilst the young roots show larger ones.

Some authors call latex an emulsion, that is to say they consider the rubber globules to be in the liquid state, just as is the tar in a tar-emulsion, or as the small fat globules

in milk are. The fact that the rubber globules are not always spherical, but often have and retain a distinctly oblong form, and sometimes even show a tail, might however serve to prove that these particles have the characteristics of the solid state, so that latex should be called a suspension.

Latex is regarded as an emulsion by Miss A. T. BORROWMANN (Lectures 1908, 243) on account of its viscosity at different dilutions. Other authors also use the term emulsion, but perhaps without making a critical difference between this and a suspension.

R. DITMAR (Kautschuk, 23), strongly opposes this view, definitely calling latex a suspension; and most recent authors hold the same view. See for instance the summary by D. F. TWISS, J. S. Ch. I. 38 (1919), 47 T. As there is no sharp limit between solids and liquids, and as the rubber globules in latex may be regarded to be in a kind of semi-liquid state, latex probably approaches a transition-form from a suspension to an emulsion.

When a coagulant is added to a drop of latex under the microscope, the lively vibrations and movements are seen to cease; gradually the globules group themselves into strings or clots, which then change into a coherent coagulum, about which we will speak in Chapter V.

A. COMPOSITION OF LATEX.

Besides rubber and water the latex contains numerous substances such as sugars, proteins, salts, resinous substances and many others. Though a considerable amount of investigation has already been done, our knowledge of the constituents of latex is still very incomplete; which fact is easily explained by the complicated nature of many of these constituents, which are often present only in small amounts. Chemically speaking, precise data about latex and its constituents are very scarce.

We now will give a summary of the composition of latex mentioning in the first place the facts that will help the reader to understand what is to follow; and, in accordance with the purpose of this book, we will pay special attention to what is known of the influence of these constituents on the properties of the rubber.

§ 2. The rubber-hydrocarbon.

By its decomposition-products the rubber-hydrocarbon is known to be an isoprene-derivative; but its exact composition and structure are still unknown. Some authors regard the rubber-hydrocarbon, and especially its degree of polymerisation, as of prime importance for the quality of the product. A highly polymerized hydrocarbon is said to give a strong rubber, whilst depolymerisation is supposed to be the cause of weaker rubber. Investigations on this point are not far enough advanced to allow of any definite conclusion; but so far as the properties of plantation-rubber are concerned, other factors certainly play at least as important a role.

The differences in rate of cure, for instance, which are the chief cause of variability in plantation-rubber, will have to be ascribed in the majority of cases to the non-rubber substances or their decomposition-products. This point will be treated elaborately in § 203.

On the other hand the possibility should not be lost sight of that very young trees perhaps produce a hydrocarbon of other composition or other degree of polymerisation than old ones; or that for instance the small rubber globules, which the microscope shows us in latex from the leaves or the small twigs (see § 1), do not contain the same hydrocarbon as the larger globules from the stem. It is not impossible that other cases of low values for the tensile strength (for instance in rubber from young plots, recently taken into the tapping round; or in rubber harvested during periods of prolonged drought) also are caused by changes in the rubber-hydrocarbon. Further research will have to clear up these points.

Whilst in former years it was generally assumed that during coagulation a polymerisation takes place, and that the rubber in the dry state is, chemically speaking, different from that in the latex, recent investigations all support the view that the rubber-hydrocarbon is present in the latex in the same form as in the rubber, and that coagulation (as far as the rubber-hydrocarbon goes) simply consists in bringing together the separate globules without further change.

The opinion of C. O. WEBER (Ber. 35 (1903), 3108), that coagulation is accompanied by a polymerisation, was opposed to by A. W. K. DE JONG and W. R. TROMP DE HAAS (Ber. 37 (1904), 3298), and by E. FICKENDEY (Z. Koll. 8 (1911), 46). See further PH. SCHIDROWITZ (Rubber (1911), page 124), and F. C. VAN HEURN (Comm. Delft I, 13), where further literature is to be found.

§ 3. The non-rubber constituents.

The non-rubber constituents of latex have an important influence on the properties of the rubber, and especially on its rate of cure and viscosity. In the study of this influence one does well to distinguish three points, viz:

1) The quantity and the ratio in which the non-rubber constituents occur in the latex—in other words: the composition of the latex.

2) The degree in which they are precipitated and kept absorbed by the rubber; that is: given a certain latex, the proportion of its non-rubber constituents that is retained by the rubber in the course of preparation.

3) The decomposition-products, which are formed from these non-rubber constituents during the process of preparation.

The first point will be treated in this chapter; the second in following chapters on different methods of coagulation and preparation. Some data on the constituents that remain in the serum after coagulation, will be found in Chapter VIII, whilst the accessory-substances in dry rubber are treated in Chapter XXI. The third point will be dealt with in Chapter VII.

We here only will give a cursory review of the non-rubber substances in latex. The first thing to state is that our knowledge about them is still exceedingly small; only a few of them are well known in composition and behaviour, the majority is ordinarily grouped under collective nouns, that serve to conceal our ignorance from a chemical point of view. As already mentioned above, in some cases it is known with certainty, in others with probability, that changes

in rate of cure have to be ascribed to the non-rubber substances; but exactly which substances have this influence, and how and in what quantities they act, has not yet been determined.

A difficulty in investigations on Hevea-latex is, that it is impossible to separate rubber and serum unchanged, because centrifugeing does not produce this result. It is necessary to effect coagulation by acetic acid or by some other foreign substance, the presence of which must be taken into account in the further investigation. Spontaneous coagulation without any addition would lead one still further astray, as it is accompanied by decomposition of serum substances, which therefore can no longer be investigated in their original form.

The following table may serve to give a rough idea of the substances that are contained in latex, and the way they are distributed between the serum and the rubber during coagulation. It is compiled for a latex which on coagulation with acetic acid appears to have a rubber-content of 30 %.

	% in the latex	Amount after coagu- lation		In rubber as % of dry rubber	In serum as % of serum
		in the rubber	in the serum		
Rubber-hydrocar- bon	28	1/1	—	92 — 94	—
Commercial rubber	30	1/1	—	100	—
Total solids. . .	33 — 34	9/10	1/10	98.8 — 99.7	5
Mineral substances (ash)	0.3 — 0.7	1/6	5/6	0.15 — 0.45	0.5 — 0.9
Components con- taining nitrogen (proteins) . . .	1 — 2	2/3	1/3	2.5 — 3.5	0.3 — 0.9
Components solu- ble in acetone (resins)	ca 2 ?	?	?	2.5 — 3.2	?
Quebrachite. . .	1 — 2	?	?	?	1.5 — 2.5
Reducing sugars .	0.15 — 0.35	—	1/1 ?	—	0.25 — 0.5

The figures represent little more than a very rough estimate; on several points the data given by different investigators show such wide divergences, that even an estimate is impossible, whilst on others no data at all are available. A complete analysis of Hevea-latex is at present still lacking; it is to be hoped that a more precise knowledge of the composition of latex will soon be gained.

Many of the best known textbooks contain figures for analyses of latex, which are of a very doubtful character. Apart from the fact that a value for „resinous” or „coloured” matter does not convey much, unless the method by which it is determined is exactly described, it is not sure that these data all relate to Hevea-latex.

For example SEELIGMANN, whose analysis (Seeligm. page 94) is everywhere quoted, — which analysis from his description on page 91 relates to a „25 year old Hevea in Brazil, tapped at 0.50 M. in September 1888”, — is supposed by J. PARKIN (Circ. R.B.G. I (1899), 145 to have confused Hevea and Castilloa-latex. The large diameter of the globules, (0.0035 mm., Seeligm. page 91), the abnormally high content of mineral matter (see below), and the specific gravity which is given as 1.019 at 14° C for 32% latex, (Seeligm. page 93) gives PARKIN a right to suppose so. This same analysis of SEELIGMANN c.s., misquoted in a report of a lecture by K.BAMBER (Ceyl. R.E. 1906, page 41; Trop. Agric. 27 (1906), 281) is found in many textbooks as a separate analysis „K. Bamber, Ceylon”, as follows:

Seeligmann, Lamy-Torrilhon et Falconnet, page 94.		The same, misstated and misquoted as „K. Bamber Ceylon”
Elastic matter	32 %	32.00 %
Organic nitrogenous matter . . .	2.30 %	2.03 %
Mineral salts (sodium and calcium, no magnesium)	9.70 %	9.07 %
Resinous matter	traces	2.03 %
Faintly alkaline water	55—56 %	55.56 %

The very high figure for mineral salts, and the stipulation that „no magnesium” is present, also make it improbable that this analysis applies to pure Hevea-latex.

The same analysis is quoted under the name of „Clouth” by HINRICHSSEN and MEMMLER (K. & Pr., page 10), whilst O. WARBURG, who quoted it in a condensed form (Tropenpfl. 2 (1898), 303), also saw it reappear under his own name.

In the same way as above the analysis of FARADAY, so often quoted as the oldest one of Hevea-latex, is believed by CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 216) on very sound reasons to have related to Castilloa-latex.

Other analyses found in literature relate to latices sent to Europe after addition of an unknown amount of preservative; often the so-called „original” latices were diluted with water. We will not quote these old data, about which no certain information is obtainable.

CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 216) mention the following analysis of pure latex from at least one hundred 10-years old trees, collected under supervision, so that in no case was any water added to the latex:

Water	60.00 %
Acetone-extract	1.65 %
Protein ($N \times 6.25$)	2.03 %
Ash	0.70 %
Sugars after inversion (calc. as glucose)	0.13 %

W. R. TROMP DE HAAS (Ann. J. Bot. 3me Suppl. I. (1910), 443) in a series of tapping experiments (see § 29) for latex from trees tapped on alternate days found the following figures (calc. on latex):

Total solids	26 — 54 %
Rubber	23½ — 48 %
Ash	0.3 — 0.7 %
Nitrogen	0.15 — 0.30 %
Resinous matter	1.3 — 3.1 %

Some other figures are mentioned in the following pages and in Chapter II.

J. PARKIN (Trop. Agric. 35 (1910), 8), basing on analyses of K. BAMBER, gives the following average composition of Hevea-latex:

Water	55—63 %
Caoutchouc	40—32 „
Resin	2.1 „
Protein	2.1 „
Ash	0.4 „
Sugar etc.	0.4 „

We will now shortly review what is known of the principal groups, and especially of their influence on the properties of the rubber.

§ 4. Mineral substances.

About the exact composition of the ash from Hevea-latex, the changes in the mineral components caused by external circumstances affecting the tree, and the distribution of the mineral substances between serum and rubber, very little is known. As indicated in the table above, the ash constitutes 0.3 to 0.7 % of the latex and mostly 0.5—0.6 %. The oxydes of potassium and sodium, form nearly half of this, and besides them are found the oxydes of magnesium and calcium, with some aluminium oxyde. In the ash of rubber some iron is generally present; but how much of these traces originates from the preparation (impure water, iron from the rolls etc.) is not known, and there is even no certainty whether pure latex contains traces of iron or not. The bases are combined with phosphoric acid, which forms approximately one fourth of the ash, and further with sulphuric acid; some authors mention also hydrochloric acid.

K. BAMBER (Circ. R.B.G. I (1899), 146) gives for a latex of 44.85 % total solids 0.405 % ash; and later (Ceyl. Adm. R. 1916, C. 9) mentions that the ash of latex contains 43 % potash and 24 % phosphoric acid.

W. R. TROMP DE HAAS (Ann. J. Bot. 3me Suppl. I, (1910), 443), in a series of tapping experiments, found 0.30—0.68 % ash in the latex.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. IX, 41; also Z. Koll. 13 (1913), 220), in the dialysate of preserved latex, found the following quantities (calculated as percentage of the latex):

	Total solids in latex	DIALYSATE						
		Total solids	Ash	SO ₃	P ₂ O ₅	CaO	MgO	K ₂ O
A	30.0	2.61	0.41	0.008	0.13	0.013	0.02	0.19
B	22.0	1.65	0.29	0.009	0.09	0.014	0.019	0.17
C	25.8	1.52	0.24	0.008	0.06	0.004	0.008	0.14
Average			0.31	0.008	0.09	0.01	0.016	0.17
in % of ash			—	2.6	29.1	3.2	5.2	54.8

The ratio of ash to total solids in the dialysate was 1 : 6.4 to 1 : 5.7. The figures have only relative value, as the amount of preservative added to the latex is not indicated.

The same authors (I.R.J. 41 (1911), 217) for pure, undiluted latex of 10 year old trees, give 0.70 % ash, and for 4 year old trees 0.24 % (compare § 24).

G. A. VERNET (Bull. I. Ch. 14 (1911), 804), in a Hevea-latex containing 45.62 % total solids, mentions the abnormally high figure of 3.35 % for ash.

F. KAYE (Rubber Ind. 1914, 139) in 100 cc. latex preserved with ammonia and containing 36.9 gms total solids, found 0.046 % P_2O_5 in the latex or 0.124 % of the total solids, whilst the acetic acid coagulum contained only 0.010 % P_2O_5 , calculated on the latex, i.e. less than $\frac{1}{4}$ of the total phosphoric acid.

W. H. ARISZ (Arch. 4 (1920), 31) in the latex of one tree found 0.60 % ash, which on continued tapping increased to 0.77 %.

An influence of the mineral substances on the properties of the rubber has not yet been reported; so far as the influence of traces of inorganic salts added to latex or rubber has been investigated, it is generally small or insignificant (compare Chapter III). That the amount absorbed by the rubber in different methods of coagulation may vary considerably (from the above mentioned normal amount of appr. 0.3 to $1\frac{1}{2}$ % and upwards) will be seen from § 88 and 90.

On the other hand, an influence on the process of coagulation by the mineral constituents is very probable (compare § 75).

CL. BEADLE and H. P. STEVENS (Z. Koll. 13 (1913), 211) found that a latex preserved with ammonia, when dialysed for two or three days, coagulated in the ordinary manner on addition of acid, so that it would seem that the soluble cristalloids play no role at all in coagulation; but on standing such latex forms aggregates or clots and does not readily coagulate with acids.

P. DEKKER (Comm. Delft I, 27), also working with a latex preserved with ammonia, found that after dialysis the latex did not readily coagulate after acidification with acetic acid, or even on boiling; but by adding a proportion of the solids from the dialysate coagulation was markedly furthered.

It may be mentioned that the ash-content of latex is certainly not constant. With heavy tapping, for instance, the ash in the serum after coagulation increases from 0.6 to 0.8 % (calculated on original serum); and as at the same time the total amount of solids in the serum decreases, the ash increases from $\frac{1}{8}$ to $\frac{1}{5}$ of the total solids.

O. DE VRIES Arch. I (1917), 279; 3 (1919), 205.

W. R. TROMP DE HAAS (Ann. J. Bot. 3me Suppl. I (1910), 443) found in several cases an increase of the ash-content in latex from trees tapped for periods of two months on alternate days, but the figures were irregular.

CL. BEADLE and H. P. STEVENS, as mentioned above, in the dialysate of preserved latex, found a ratio of ash to total solids between 1: 6.4 and 1: 5.7.

§ 5. Nitrogen derivatives.

These substances are generally indicated by the collective name of „proteins“. This, however, is not to be recommended, as it is precisely the decomposition-products of the proteins that play such an important role in vulcanisation, as will be shown in § 108 and in Chapter XXI.

Which proteins and which other nitrogen-containing substances are present in latex is still unknown. The total amount in latex is 1—2 % (see the table in § 3), corresponding with a nitrogen-content of 0.15 — 0.3 %.

J. PARKIN (Ann. Bot. 14 (1900), 198) mentions analyses made by K. BAMBER, showing a nitrogen-content corresponding to about 2 % of protein in Hevea-latex.

P. v. ROMBURGH (Med. Pl. 39 (1900), page 94) mentions 0.25 % nitrogen or 1.6 % proteins in latex.

W. R. TROMP DE HAAS (Ann. J. Bot. 3me Suppl. I (1910), 443) found in a series of tapping experiments 0.15—0.30 % of nitrogen in the latex of trees tapped on alternate days for periods of two months.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 41; also Z. Koll. 13 (1913), 220) in preserved latex found, on a total of 1.21—1.56 % proteins, 0.87—1.26 % non diffusible and 0.27—0.34 % diffusible nitrogen-derivatives (calc. by the factor 6.25 from the N-content), or $\frac{1}{5}$ to $\frac{1}{4}$ diffusible.

P. DEKKER (Comm. Delft I, 24) also stated that part of the nitrogenous substances can be removed from latex by dialysis; in a latex preserved with ammonia he found this part to be less than 0.4 % (calc. as proteins on the latex).

G. A. VERNET (Bull. I. Ch. 14 (1911), 804) gives 2.30 % of albuminoids in a latex of 45.62 % total solids.

W. H. ARISZ (Arch. 4 (1920), 31) in latex of one tree found 0.28 % nitrogen, which on continued heavy tapping decreased to 0.18 %.

The presence of *ammonia* in the serum after coagulation with acetic acid was reported by K. GORTER (Arch. I (1917), 376), who identified it after distillation with magnesium oxyde in the form of its platinic chloride doublesalt.

It is worth while to note that, though part of the proteins in latex may be absorbed or bound by the rubber globules, another part is certainly in solution in the serum, and remains dissolved in it after coagulation. The table in § 3 indicates that in coagulation with acetic acid approximately $\frac{2}{3}$ of the nitrogen-compounds are absorbed by the rubber and $\frac{1}{3}$ remains dissolved in the serum.

J. PARKIN (Circ. R. B. G. I (1899), 151) already stated that not all the protein from latex is precipitated by acetic acid, but that part of it remains in the serum.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 18; also Z. Koll. 13 (1913), 208) found 8.48 % of proteins in the solids from a certain latex (preserved with formalin) when evaporated to dryness; 4.28 % were found in the clot coagulated with alcohol and 3.06 % in the precipitate caused by formalin on keeping. The same authors (l.c. page 43 resp. 220) found 5.1 to 5.5 % of proteins in the solids from preserved latex; and as ordinary rubber generally contains 2.8 % of proteins, they conclude that only about half of the proteins from latex is retained by the rubber.

B. J. EATON and F. W. F. DAY (Agric. Bull. F. M. S. 4 (1916), 350; Bull. F. M. S. No. 27, 101), in latex diluted to a rubber-content of 16.9 % (by weight), found 0.11 % nitrogen, whilst the air-dry crepe contained 0.40 %, from which it may be calculated that the rubber contained 61.5 % of the total nitrogen in latex.

The serum contains an accelerator, which is found in the sticky hygroscopic residue after evaporation, the presence of which will be further discussed in § 112. Whether this accelerator is a nitrogen-derivative (for instance an amine such as di- or trimethylamine), remains to be investigated.

The nitrogen-derivatives are supposed by many authors to play an important role in latex as a stabilising colloid or as a film surrounding the rubber globules; coagulation is said by some to be in the first instance a precipitation of the proteins. We will treat this point in § 77; but we may here mention that the influence of the removal of the proteins on the stability of the latex is by no means cleared up.

D. SPENCE (Lectures 1908, 195), probably working with preserved latex, could remove more than half of the proteins in Hevea-latex after digestion with trypsin, without coagulation taking place.

H. C. T. GARDNER (Lectures 1908, 227), on dialysing the soluble albumins after having treated the latex with papain, obtained on the membrane a film of caoutchouc, consisting of separate particles without coherence which however on kneading gave the usual tenacious mass, proving that the coherence in the coagulated clot is not dependent upon a film of proteins.

A. J. ULTÉE (Teysm. 28 (1917), 179) obtained coagulation in an acid and even in an alkaline medium by adding papain to the latex (compare § 104).

§ 6. Components soluble in acetone.

The acetone-extract of dry rubber, generally called „resin“, plays an important part in its analysis, especially when types other than Hevea-rubber are concerned. It is well known that part of this extract is soluble in water, and that it also contains nitrogen-derivatives, so that a clear differentiation from other groups of components is not obtained in this way (compare Chapter XXI).

In latex, however, these substances have been only slightly investigated; little is known about their presence in latex and about the acetone-soluble matter that remains in the serum.

This much may be said, that in the acetone-extract of the solids obtained from evaporated latex, one may expect to find besides resinous substances also quebrachite, which is soluble in hot acetone, when this solvent contains some water.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. XXV, 581) tried to separate the resins from latex by extraction with ether; the proportion, in which caoutchouc and acetone-soluble substances were extracted, remained however nearly the same in successive extractions.

G. A. VERNET (Bull. I. Ch. 14 (1911), 804) gives in a latex, containing 45.62% total solids, an amount of 0.62% of resins soluble in acetone.

P. DEKKER (Comm. Delft I, 24), in the dialysate of a latex preserved with ammonia, found 0.66% (calc. on the latex) to be soluble in acetone; by heating the solids from this dialysate with hydrochloric acid, the acetone-soluble components increased to 1.59%.

A better knowledge of the real resinous substances would be interesting in many respects; perhaps among them there may be some which play a role in the formation of the rubber-hydrocarbon by the tree; or they may partly constitute decomposition-products of the rubber.

See f. i. D. SPENCE, Lectures 1908, 194.

F. W. HINRICHSSEN and J. MARCUSSEN (Z. angew. 23 (1910), 49) drew attention to the fact that the decomposition-products of the rubber-hydrocarbon must, as this hydrocarbon itself, be optically inactive; as is the case with the „resins” in Hevea-rubber. The optically active resins found in other rubbers than Hevea must constitute plant-products formed in addition to and not from the rubber-hydrocarbon.

§ 7. Quebrachite.

One of the few constituents of latex, about which details are known, is quebrachite, a substance found in the latex to an amount of 1—2%, which during coagulation remains for the greater part in the serum, in which it forms nearly half of the solids.

Quebrachite, chemically speaking, is 1-methylinositol $C_6H_{11}O_5OCH_3$ with a melting point of 191° and a specific rotatory power $a_D = -80^\circ$. Though not a „sugar” in the chemical sense of the word, it has a sweet, sugar-like taste, is easily soluble in water, but not easily soluble in alcohol, acetone and ether.

A. W. K. DE JONG (Rec. 25 (1906), 48) isolated quebrachite from Hevea-latex after coagulation with alcohol.

PICKLES and WHITFIELD (Proc. 27 (1911), 54; Gard. Bull. I (1912) 152; Bull. Imp. Inst. 10 (1912), 27) state that they have isolated quebrachite (0.46 % of the total latex) from a specimen of latex from one tree in the Botanical Gardens at Singapore, „in the aqueous portion of the latex, after separating the rubber”.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. IX, 41; also Z. Koll. 13 (1913), 221) estimate the amount of quebrachite in the dialysate of latex at 0.8—1.6% (calc. on the latex), but these figures, being the „difference unaccounted for by constituents separately determined”, lack the value of positive proof.

K. GORTER (Arch. 1 (1917), 376) in serum of a latex containing 37 % rubber, after coagulation with acetic acid, found appr. 1.5 % quebrachite calculated on the latex, or 50 % of the total solids in the serum (compare § 111).

The amount of quebrachite in latex is nearly constant; it is somewhat higher, when tapping is begun on trees that have had a rest, but seems to be little influenced by other factors and remains in the neighbourhood of 1.5 % of the latex.

§ 8. Sugars.

Besides quebrachite latex also contains small quantities of the ordinary sugars. Their amount may be some 0.3.—0.4 % in latex from bark recently taken into tapping; in ordinary tapping some 0.2 % may be present, whilst with heavy tapping or during the wintering period these sugars may for the greater part disappear.

The identity of these sugars has not yet been determined.

As they are very soluble in water, during coagulation the greater part of them remains in the serum; in rubber they have not yet been identified with certainty.

The data about these substances in literature are often somewhat vague. When the method of determination is not indicated, no conclusions are possible as to what was really determined. When using the rotatory power, quebrachite and proteins, which also deviate the rays of light, should be removed first; when using the reduction of Fehling's solution, other substances complicate the result.

K. BAMBER (Circ. R. B. G. I. (1899), 146), in latex from one tree at Peradeniya, found 0.36 % sugar (calc. as cane sugar, in % of the latex).

G. A. VERNET (Bull. I. Ch. 14 (1911), 804), in his already often quoted analysis, gives 1.43% of sugars, without further details. He further (Bull. Mars. 1 (1919), 117) mentions that when the trees are only recently taken into tapping, the latex may contain 3% of sugars (not specified).

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 41; also Z. Koll. 13 (1903), 221), in the dialysate of preserved latex, found 0.15–0.24 % of sugars after inversion (calc. on the latex), and (I. R. J. 41 (1911), 217) in latex evaporated to dryness 0.12 % for 10 year old, and 0.22 % for 4 year old trees, calculated as glucose on the latex, and determined, after inversion, by their reducing action on Fehling's solution. (It is however to be taken into account that part of the sugars may have been destroyed by evaporating the latex to dryness).

It is worth while to state that in Hevea-latex (as distinct from other species) no starch ever occurs.

§ 9. Acids.

The prevalence of inorganic bases over inorganic acids in the ash of latex points to the fact that the bases are partly saturated by an organic acid, which however has not yet been identified.

K. GORTER (Arch. I (1917), 376), in the solids from the serum, isolated a non-volatile organic acid, soluble in ether, the nature of which could not yet be determined. Volatile organic acids were not present.

The reaction of latex, as it exudes from the tree, is nearly neutral. Some authors mention a slightly alkaline reaction, whilst others state positively that the reaction was found to be slightly acid. It will be interesting to investigate the degree to which this divergency bears a relationship to physiological and other factors.

Alkalinity in freshly tapped Hevea-latex was mentioned by SEELIGMANN c. s. (Seeligm. page 94) and R. H. BIFFEN (Ann. Bot. 12 (1898), 167). The Government Chemist at Singapore found Hevea-latex distinctly alkaline, in contrast to the latex of all other laticiferous trees in the Gardens (Ann. Rep. Bot. Gardens Singapore 1903, page 7; see also Trop. Agric. 23 (1904), 774). H. P. STEVENS (VIII Int. Congr. 9, page 17; also Z. Koll. 13 (1913), 207), during his stay in the East, found the fresh

latex occasionally distinctly alkaline, and G. S. WHITBY (VIII Int. Congr. 25, 597; also I. R. J. 45 (1913), 941 and Z. Koll. 12 (1913), 147) states that careful testing of latex immediately upon its issuance from the tree, will show it to be faintly alkaline, whilst within a short time (say half an hour) the latex is faintly acid.

On the contrary J. PARKIN (Circ. R. B. G. 1 (1899), 144) could never state alkalinity by using red litmus paper; P. VAN ROMBURGH (Med. Pl. 39 (1900), 93) found the latex slightly acid, and the same was held positively to be always the case, against all contrary statements, by G. A. VERNET (Bull. I. Ch. 14 (1911), 804 and 808), who gives an amount of 0.012 % calculated as acetic acid (that is only 0.12 cc. strong acid per liter) in a latex of 45.62 % total solids.

W. BOBILIOFF Sr. (Arch. 3 (1919), 408 and 411) found the reaction to litmus more or less acid or in some cases neutral, but in these latter cases the reaction to phenolphthalein (when titrating with $\frac{1}{10}$ N sodium hydroxyde) was found to be slightly acid; the fresh latex was stated to be 0.003—0.018 N, corresponding with 0.18—1.08 gm acetic acid per liter of latex.

The acidity of latex, after it has exuded from the tree, rapidly increases; we will treat this in § 13.

§ 10. Other organic compounds.

It may be mentioned that traces of hydrocyanic acid (HCN), and acet-aldehyde (C_2H_4O) have been proved to be present in latex.

M. KERBOSCH (Med. Rubber III (1914), 2; Rubb. Rec. 1914, 361) after steam-distillation of latex isolated acet-aldehyde in the form of its para-nitrophenyl hydrazone with a mp of 128° ; in ordinary latex he found 0.006 gr. of acet-aldehyde per liter of latex, but during wintering the amount was much smaller.

Whilst acetone and hydrocyanic acid have been proved to be present in the leaves, flowers and fruits of *Hevea* by P. VAN ROMBURGH (Ann. J. Bot. 16 (1899), 1; Med. Pl. 39 (1900), 84) and in the form of phaseolunatine were found in the seeds by K. GORTER (Rec. 31 (1912), 264), M. KERBOSCH (l. c.) could not find acetone in latex, but distinctly proved the presence of hydrocyanic acid.

The smell of methylamine was noted in fresh latex by SEELIGMANN c.s. (*Seeligm. page 93*); in § 5 we already mentioned that traces of ammonia have also been found.

§ 11. Yellow substances.

The colour of latex may vary considerably, from yellowish to bluish white. Apart from the change caused by dilution (the larger the degree of dilution, the more the colour of the latex and also of the crepe changes from yellowish to bluish) the colour of pure original latex may be very different. Latex from untapped bark is often more or less yellow coloured, and this colour remains in the crepe, which often is decidedly saffron yellow; in the brown smoked sheet it becomes invisible. When the trees are tapped regularly, the latex in most cases loses this yellow tint some days or weeks after tapping was started (compare § 29); but some trees continue to give yellow latex indefinitely.

See for instance G. S. WHITBY, *Ann. Bot.* 33 (1919), 321.

J. PARKIN (*Circ. R. B. G. I* (1899), 144) stated that from 32 trees in Peradeniya 9 had a decidedly cream-coloured latex. The frequency on plantations is however much less than this and certainly below 1 % of the trees.

That ordinary latex also contains this yellow substance to a certain degree, is evident from the fact that it accumulates in the first clots in cases of partial coagulation, when the yellow or yellow-brown colour becomes very apparent, at least when no oxydase is present to cause the rubber to turn dark-brown.

About the composition and formation of this yellow substance nothing is known as yet; and the same is the case with its possible influence on the properties of the rubber.

§ 12. Enzymes.

Enzymes are very generally found in plant juices, and their presence may be expected in latex also. Research work on this subject is still rather incomplete; even the question whether latex in the latex vessels themselves contains enzymes, or whether these originate from other cells opened during tapping, is not yet settled.

G. VERNET (Bull. Mars 1 (1919), 111) draws attention to the peroxydase present in the tissues outside the latex vessels, and (ibid. page 118) also mentions peroxydases secreted by aerobic micro-organisms as a possible source.

Amongst the enzymes which are supposed to be present in latex, a certain rôle is said to be played by a coagulating enzyme. Definite proof of its presence is, however, still wanting; the enzyme has not yet been isolated in a pure state, and whether its existence must necessarily be assumed in order to explain the phenomena of coagulation still remains to be seen (see § 78).

More certainty exists about the presence of an oxydising enzyme. The formation of a violet coloured substance on the surface of the coagulum, the darkening of rubber, especially of the lower grades, and many closely connected phenomena have been with certainty traced to the action of an oxydising enzyme.

This may be either an oxydase or a peroxydase, the latter giving only oxydative discolourations in the presence of a peroxyde such as hydrogen peroxyde, the former acting without such an addition.

The exact nature of the oxydising enzyme or enzymes in latex has not yet been determined with certainty; the principal phenomenon, the violet discolouration of the coagulum, may be assumed to be caused by a substance of the tyrosinase type, producing by oxydation melanin-like substances with at first a pink later a violet and finally a blue-black colour.

The literature on this subject is rather confused and often contradictory; in fact, the different reactions on oxydising enzymes require some care in the handling.

D. SPENCE (Biochem. Journ. 3 (1908), 351; see further Lectures 1908, 196) mentions the presence of an oxydase in different samples of preserved latex received from Ceylon and dialysed for 24 hours. It was of the oxygenase type, giving reactions with the indophenol mixture of RÖHMANN and SPITZER, with hydrochinon, and with p-phenylene-diamine in the absence of hydrogen peroxyde, and still more marked reactions when

hydrogen peroxyde is present. After diluting the latices with water and coagulating with 40% alcohol, a gummy mass could be precipitated from the serum by absolute alcohol, which gave the reactions of a powerful oxydase.

V. CAYLA (J. d' A.T. 8 (1908), 335) mentions that, in accordance with the results of PH. SCHIDROWITZ and F. KAYE (I.R.J. 34 (1907), 24), he could find no oxygenase in latex preserved with ammonia, nor in fresh latex drawn from a Hevea cultivated in Europe in a glass house. He draws attention to the importance of investigating such points always in loco with fresh latex. CAYLA, at first, could find no reaction for peroxydase (C. Gp. 1908, 2185), but later on (I. R. J. 39 (1910), 563) regards the presence of a peroxydase as certain.

B. J. EATON (Bull. F. M. S. No. 17 (1912), 30) showed that the addition of oxydisable phenols, such as amidol, hydroquinone and p-phenylene-diamine to latex causes rapid darkening in the coagulum obtained by acetic acid, which discolouration could be prevented by adding a small amount of bisulphite or by excluding the air.

G. S. WHITBY (VIII Int. Congr. 25, 599; also I. R. J. 45 (1913), 941 and Z. Koll. 12 (1913), 149) stated the presence of a peroxydase in fresh latex under many different conditions, e.g., condition of bark, tapping system, etc., but could never obtain a reaction for oxygenase in fresh latex, not even from trees giving „black latex”.

K. GORTER (Teysm. 23 (1912), 44) supposed tyrosinase to cause the discolouration in coagulum and rubber, which was further proved by A. W. K. DE JONG (Mededeelingen van het Agricultuur-chemisch Laboratorium, Buitenzorg, X (1915), page 48).

In studying these phenomena it should, of course, be taken into account that an oxydation (violet discolouration) is only obtained when both enzyme and oxydisable substance are present. To state the presence of the enzyme, one has to proceed in a special way, adding the oxydisable substance (for instance tyrosin). For estate practice, however, the tendency toward oxydation is the only point of importance, so that „oxydase” and „oxydisable substance” are often treated under one head.

That the tendency toward oxydation may differ considerably, is very apparent when scraps from different trees are inspected. The remnant of latex that solidifies on the tapping cut, the so-called tree-scrap, is on some trees pure white or yellowish, on others very dark. It is well known to planters that the strong tendency toward violet disco-

louration, shown at certain times by the coagulum, may be caused by the latex from a relatively small number of trees, which give the so-called black latex.

G. S. WHITBY (Ann. Bot. 33 (1919), 321) mentions a tree that produced „black latex” during a period of five years and always gave an exceptionally strong reaction for peroxydase.

Higher up the stem the tendency to oxydation (discolouration) is generally stronger than below, which may be very apparent from scraps on tapping cuts at different heights. Rapid discolouration may be associated merely with insufficiently deep tapping; often the latex at the upper end of the tapping cut, where tapping is shallow, darkens rapidly. In untapped bark the tendency toward discolouration is often greater than in bark that is regularly in tapping. A change of tapping surface, therefore, is often accompanied by a stronger tendency toward discolouration because new bark is opened and the cut is transferred to a position higher on the tree.

See f.i. S. MORGAN, Prep. Pl. Rubber page 39; G. S. WHITBY, VIII. Int. Congr. 25, 600; also I. R. J. 45 (1913), 942 and Z. Koll. 12 (1913). 149; further Ann. Bot. 33 (1911), 321.

A. W. K. DE JONG (l. c.) also stated that latex from higher cuts shows a stronger tendency toward oxydation than latex from lower cuts; by adding tyrosin to the last named latex he proved that the oxydising enzyme is present, but the oxydisable substance is absent in such cases. In a ringed tree the latex from bark above the ring contained tyrosinase and a tyrosine-derivative, and blackened quickly; latex from bark below the ring contained only tyrosinase and gave a discolouration only after addition of tyrosin.

J. PARKIN (Ann. Bot. 14 (1900), 200) found the latex from seed-capsules to darken always rapidly, whilst the latex from young shoots blackened sometimes, and the latex from the stem, if kept free from micro-organisms, did not darken.

It may further be mentioned that during and after wintering the latex often shows an increased tendency toward discolouration (compare § 21).

For the ordinary course of preparation, however, these facts have lost much of their importance, since in bisulphite such

an excellent means has been found to prevent surface oxydation (see § 48).

It may be worth while to mention that sodium bisulphite does not bleach the dark, melanin-like substances when they are once formed; it acts in such cases as an anti-oxydant, preventing oxydation, and not as a bleaching agent.

On the prevention of the action of oxydases by means of heating see § 100 and 140.

The discolouration is influenced by the degree of acidity of latex or coagulum, as will be discussed in § 107.

The dilution of the latex may also have an influence, whilst the tendency toward discolouration may be greatly augmented by adding substances such as calcium chloride (see § 90) and others.

Though the discolouration may be very visible, and the streaks caused in pale crepe by the thin discoloured surface layer of the coagulum may decrease its value from a market point of view, it has not yet been possible to detect any influence of this violet oxydation layer on the properties of the rubber; but then it should be remembered that the actual amount of violet oxydation products is only small.

See G. S. WHITBY, J. S. Ch. I. 35 (1916), 497; also I. R. J. 51 (1916), 792.

During coagulation a large part of the substances causing discolouration is precipitated with the rubber; and especially the first clots contain a large proportion of them. Previously formed clots or lumps in the latex, if not removed by straining, cause streaks or discoloured spots in the finished crepe; and partial coagulation gives a highly coloured rubber from the first clots, whilst the rest gives a very pure white crepe—a method formerly used to obtain pale rubber (see § 176).

Part of the substances causing oxydation however remains in the serum, which may darken considerably when kept in contact with the air.

§ 13. Changes in composition of the latex.

The moment the latex exudes from the tree, different changes begin to take place. For a large part these are due to bacterial action, and the most pronounced of them is the increase in acidity. Latex tapped at 7—8 a.m. and tested at the laboratory at 10 a.m. may show an acidity of 0.03 N, corresponding with 1.8 gms of acetic acid per liter of latex; and in the course of 3 hours the acidity may increase to 0.04 N or 2.4 gms of acetic acid, before coagulation or even clotting sets in.

W. SPOON, Arch. 3 (1919), 331 and 337.

The acids formed have not yet been investigated, but probably they are the same as those formed during spontaneous coagulation (lactic acid, some acetic and traces of succinic acid, see § 94 — 96).

These changes after a shorter or longer time lead to spontaneous coagulation or to clotting and flocculation. In general practice, to avoid spotting and discolouration in the finished product, the time between the tapping and the coagulation in the factory is always made as short as possible.

Besides the increase in acidity other still unknown changes may perhaps occur in latex on standing, but as far as investigated they have practically no influence on the properties of the rubber, which are the same whether the latex is coagulated immediately or some hours after tapping.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 500; also I.R.J. 51 (1916), 830) found only a very slight increase in rate of cure in rubber from undiluted latex kept for 5 hours before coagulation.

Practically as soon as it exudes from the tapping cut and comes into contact with the outer world, latex is contaminated with bacteria, which rapidly multiply, feeding on the serum-substances, and cause the above mentioned changes in latex, and also different changes in the coagulum,

which will be treated in § 107. In all, 27 species have been isolated, of which one forms acids from the sugars, whilst the others decompose proteins or liquify gelatine.

DENIER et VERNET, C. R. 165 (1917), 123; G. VERNET, Bull. Mars. 1 No. 3 (1919), 114.

The changes accompanying spontaneous coagulation will be treated in § 94 — 96.

§ 14. Rubber-content of latex.

For the rubber-content of latex, as it arrives at the estate-factory, largely diverging figures are found. In former years, when the latex was washed down the cut with water, a latex containing only 10 % of rubber, and even less, was quite common, and not every planter was easily convinced how lavishly his coolies had used water in collecting the latex. Even now a latex containing 25 or 20 % of rubber is often quite erroneously regarded as undiluted, and by many it is not realised to how large a degree the latex may be diluted by apparently unimportant factors.

Even when no intentional addition of water to the latex takes place—by adding to the latex the water used to clean the cups, or by fraud (coolies paid by the quantity of latex and aiming at an increase of it)—, there are many ways in which the latex may be diluted to some extent. Apart from rain during tapping or collecting, drops falling from the leaves, stems that are still wet from rain during the night, we may mention the use of anti-coagulants in pails or cups; further pails or cups that are still wet from the cleansing of the foregoing day etc. How important such generally neglected factors may be, will be seen from the fact that in aluminium cups, with some water adhering on and between the cups as they are carried, nested one within the other, to the field, we collected water to an extent of $\frac{1}{8}$ and even $\frac{1}{4}$ of the volume of latex to be expected. A latex of originally 35% would by that seemingly unimportant cause be diluted to 30½ or 26 % respectively. When collecting data on pure original latex, special care and supervision are necessary, that the latex really in no way becomes diluted. For most of the figures contained in present literature no certainty on this point is obtainable.

We will make some remarks about the dilution of latex in the field and in the factory in § 39 and 64—69, and here only treat the rubber-content of pure, original latex, which may vary considerably.

The highest rubber-content stated in present literature seems to be approximately 60 %.

P. VAN ROMBURGH (Med. Pl. 39 (1900), 94) mentions 60 % in the dry monsoon. T. PETCH (Bull. Ceyl. 42 (1919), 6) found figures up to 62 %, with the restriction, however, that the latex may have been concentrated by evaporation. A. E. COLINS (I. R. J. 43 (1912), 99 and 44 (1912), 707), for two 30 year old trees, mentions 50—70 % dry rubber in the latex of the first few tapplings.

The lowest rubber-content in undoubtedly undiluted latex is 3.77 % (W. BOBILIOFF, *Arch.* 3 (1919), 396) and was obtained by regularly tapping an isolated piece of bark, that is a piece surrounded by a cut severing all latex vessels, so that no flow of latex from the surrounding bark is possible. In other such cases rubber-contents of 6.8—10 % were often noted.

The low figures mentioned by PH. SCHIDROWITZ and F. KAYE (I. R. J. 31 (1907), 24; J. S. Ch. I. (1907), 935; *Rubber*, page 121), viz. 4.6 % in latex from upper bark of 5 year old *Hevea* in Ceylon, and by H. P. STEVENS (I. R. J. 1907; see WRIGHT, page 258) relate to preserved latex diluted to an unknown extent (compare WRIGHT, page 258). The abnormally low content of total solids (only 0.05 %) in the serum of SCHIDROWITZ and KAYE's 4.6 % latex indicates that this latex was strongly diluted with water.

Latex from untapped bark or from trees that have had a period of rest shows a high rubber-content, generally 45 % or more; after tapping is started, the rubber-content falls and after some days or a few weeks reaches the value which represents the equilibrium between the state of the tree and the tapping to which it is subjected.

As an example of these changes the following figures may serve for trees tapped daily with two cuts on $\frac{1}{4}$ circumference:

2 nd day	44.0	%	
3 ^d "	39.4	"	
6 th "	35.0	"	
9 th "	33.8	"	
13 th "	30.4	"	
16 th "	29.6	"	
20 th "	28.0	"	
25 th "	26.4	"	
5 th week (average)	25.3	"	} <i>State of equilibrium.</i>
6 th " "	24.6	"	
7 th " "	25.7	"	

The rubber-content therefore falls in the course of four weeks from 44 % to nearly 25 %, which represents the state of equilibrium, and at which figure it remains.

A. E. COLLINS (I. R. J. 44 (1912), 707) mentioned a decrease in rubber-content of the latex from 69.5 % to 27.2 % in the course of 3½ weeks, for two old trees taken into tapping just before wintering.

The changes in latex after opening a tapping cut will be treated further in § 29.

It is to be remarked that the rubber-content on the first day (or on the first two days), when starting tapping, is often found to be much lower than on the following days.

Apart from a large percentage of lump, which is often formed in the latex from a newly opened cut, and tends to lower the percentage of rubber in the remaining latex, the here meant low rubber-content is probably connected with the fact that the tapping cut does not always immediately reach its final depth, and is mixed with saps from other than the latex vessels. A closer study of this phenomenon might be interesting in many respects. For examples see R. H. LOCK and M. K. BAMBER, Circ. R. B. G. 5 (1911), 319 and 322; O. DE VRIES, Arch. 2 (1918), 449; 3 (1919) 131, 133; J. G. J. A. MAAS, Arch. 3 (1919), 307.

Whilst the figures given above may be regarded as representative for the general trend of affairs on estates, it should not be forgotten that such figures, giving the average properties of a large number of trees, by no means hold good for every separate tree, investigated individually. In such cases the rubber-content may diminish in the course of tapping, but it also may remain nearly constant. The following figures for trees in one row may be quoted:

Tree	1	2	3	4	5
First week	44.2	38.6	47.4	43.0	44.4
Second „	45.6	37.8	40.9	33.2	44.8
Third „	41.4	36.5	35.6	28.0	41.8
Fourth „	38.2	35.7	32.3	25.7	40.9

Whilst trees 3 and 4 show a regular decrease in rubber-content on continued tapping, the difference for the other trees is so small that the rubber-content may be regarded as nearly constant.

The rubber-content of latex, in the state of equilibrium which we have already spoken about, is dependent upon the tapping system; other circumstances being equal, it is the lower, the heavier the tapping. As example the following figures for groups of trees in one plot may be mentioned:

1 cut on $\frac{1}{3}$ circumference	33.6 ⁵ ‰
2 cuts „ $\frac{1}{4}$ „	31.2 „
2 „ „ $\frac{1}{4}$ „	29.1 ⁵ „
2 „ „ $\frac{1}{2}$ „	26.6 „
2 „ „ $\frac{3}{4}$ „	22.6 „
2 „ „ $\frac{1}{1}$ „	22.2 ⁵ „

See O. DE VRIES, Arch. 3 (1919), 202.

Other factors, which put a heavier stress on the tree, act in the same way in lowering the rubber-content of latex. For instance, when the trees are pollarded before thinning out, and the pollards tapped for some time on the system formerly used:

before pollarding	25.8 ‰
after pollarding	21.1 ‰

O. DE VRIES, Arch. 2 (1918), 254.

On the other hand, factors that improve the condition of the trees, tend to increase the rubber-content of the latex by one or more percent. Such factors are, for instance, a short rest caused by a holiday or by the sickness of a tapper; shallow tapping; tapping on alternate days instead of every day, etc.

O. DE VRIES, Arch. 2 (1918), 453; 3 (1919), 202. For further details see § 30—32.

T. PETCH (Bull. Ceyl. 42 (1919), 6) gives a rubber-content of 30.2% for tapping thrice per week, 38.2 % twice per week and 41.3% when tapping only once per week, but it is not certain that the figures represent the rubber-content of original unchanged latex.

K. BAMBER (Trop. Agric. 49 (1917), 324) mentions 29.1 % for daily tapping as compared with 32.0% for tapping on alternate days. No certainty however is given that these figures relate to pure, undiluted latex.

Apart from the treatment to which the tree is subjected the state of the tree itself also has an influence, which may be very large. We already have mentioned above two groups of trees tapped on the same system (2 cuts on $\frac{1}{4}$) and giving—for unknown reasons—a rubber-content of 31.2 and 29.15%. For individual trees from the same plot the differences may be much larger. So five trees, tapped on the same system, gave us as an average of several determinations:

19.4 29.5 31.1 31.4 35.6 %

whilst in a plot giving a monthly average of 34.5 %, one tree tapped on the same system gave an average of 16.9 %.

G. S. WHITBY (Ann. Bot. 33 (1919), 314) gives figures for the rubber-content in latex of 245 seven year old trees from one field. Whilst the mean is 36.58 %, the extremes are 23 and 55 %, and the figures show approximately a symmetrical variation-curve. The rubber-content of the latex from individual trees was found to be fairly constant over long periods.

The rubber-content further shows seasonal variations; for instance, for one group of trees the rubber-content of the pure latex in successive months was:

April (wet)	32.6 %
May	33.6
June	34.4
July (dry)	34.5
August (dry)	33.0
September	32.0
October	32.4
November (wet)	32.0

December (wet)	31.5 %
January (wet)	31.3 „
February (wet)	31.9 „
March (wet)	31.8 „

therefore a difference of 2 % between the wet and the dry monsoon.

A difference in rubber-content of the latex, caused by the monsoon, is well known in estate-practice; but the figures obtained for latex, as it arrives at the factory, often show this difference to an exaggerated extent. In the wet monsoon it is often impossible to avoid dilution of the latex, whilst in the dry monsoon concentration by evaporation (heat and wind) may play a rôle. Larger differences than the above may perhaps be expected in regions with a more pronounced dry monsoon. Individual trees sometimes will show in a more pronounced way the influence of wintering etc.; such differences are averaged up in mixed latex from rather large groups of trees, because the trees do not winter all at the same time, but gradually over a period of 1—3 months.

We have treated the differences in rubber-content at some length, as they may be of importance in connection with the properties of the rubber. The physiological factors which cause the rubber-content to increase or decrease, may effect a change in composition of the latex (or better of the serum); the very little we know about this will be given in Chapter II.

Apart from this factor, however, assuming the composition of latex and serum to remain the same, the rubber-content of latex is of importance for estate-practice, as the latex is generally diluted with water to a standard rubber-content. The higher the rubber-content of the original latex, the more water will be necessary to bring the latex, say, to 15 %, and the more dilute the liquid, from which the rubber is coagulated, will be in serum-substances, which further causes smaller quantities of serum-substances to be absorbed by the rubber from this dilute fluid. As the serum contains an accelerator, this results in a slower curing rubber, the more the latex is diluted. We will treat this influence of diluting the latex in § 64.

B. PHYSICAL PROPERTIES OF LATEX.

§ 15. Specific gravity.

Specific gravity in the following is always expressed taking that of water of the same temperature as 1.000, i.e. d_4^t and not d_4^t or d_0^t .

The specific gravity of latex plays an important rôle in so far as densimeters have been and still are largely used to determine the rubber-content and to reach a standard dilution. We will treat this aspect of the question in § 56—62.

Latex being a mixture of rubber globules and of serum, the specific gravity is given by the specific gravities of both constituents, and by the ratio in which they are mixed.

Whether the simple law of mixtures is strictly applicable in this case, still remains to be investigated. On theoretical grounds deviations are to be expected, as the rubber globules will absorb serum-constituents; but as far as data are available the influence of these absorption-phenomena on specific gravity may be neglected for all practical purposes. Dilution of latex with water gives specific gravities following as nearly the straight line assumed by the law of mixtures, as the unavoidable errors of observation would lead one to expect. Even when coagulating latex with increasing amounts of acetic acid and calculating the specific gravity of the original serum from the different acid sera, practically the same figures are obtained, so that the deviations caused by absorption-phenomena or chemical changes even in such cases are negligible.

B. J. EATON (Bull. F. M. S. No. 17 (1912), 49) found the specific gravity of latex on dilution with water on the average to follow very nearly the straight line. See also O. de VRIES, Arch. 3 (1919), 189 and 204; 1 (1917), 248 and 275.

The specific gravity of the rubber globules in latex is not yet exactly known; it lies in the neighbourhood of 0.915, and for ordinary latex is probably near 0.914. For latices with a low rubber-content a somewhat higher specific gravity for the rubber globules was found (by calculation), but this needs further corroboration. Of course the specific gravity of rubber in latex on theoretical grounds may vary somewhat with the constitution of the rubber (differences in caoutchouc-hydrocarbon, resins, proteins, etc.) and with varying absorption-

phenomena. For practical purposes it may however be regarded as constant; in Fig. 1 0.914 is chosen for it.

O. DE VRIES, Arch. 1 (1917), 278 and 3 (1919), 191 and 205.

The specific gravity of the serum shows marked variations, running parallel with changes in its composition (content of different substances such as proteins, sugars, mineral substances, and so on). Whilst a review of the composition of the serum is given in § 3 and 111, the influence of the most important factors in tapping and in the condition of the trees will be treated in Chapter II. We here only mention that the specific gravity of the pure, original serum under different circumstances was found to vary between 1.025 and 1.016.

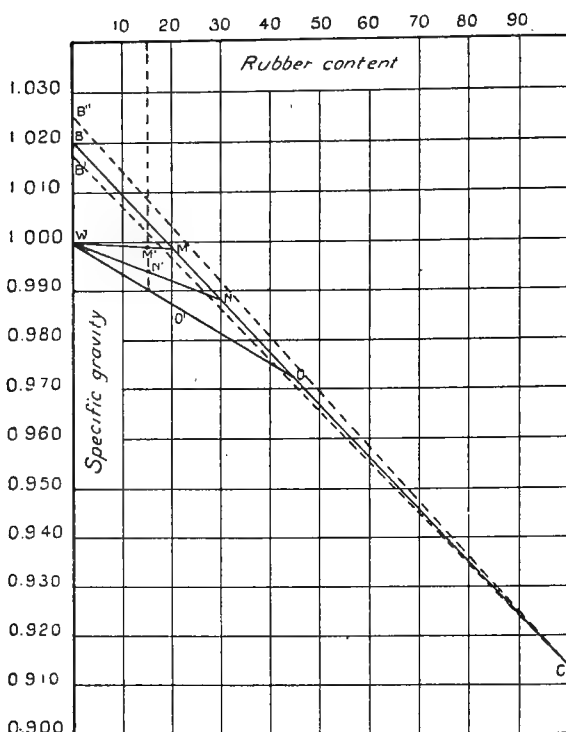
O. DE VRIES, Arch. 3 (1919), 202.

Now taking 0.914 as the normal figure for the rubber globules, and 1.020 as a normal value for serum from ordinary latex, the straight line that joins B and C in Fig. 1 gives the specific gravity for latices of different rubber-content. A latex with 45 % rubber (point O) will show a specific gravity of 0.972; 30 % rubber will give a latex of 0.988, and latex with as low a rubber-content as 20 % will show a specific gravity of 0.999.

In reality, such large changes in rubber-content are not found without changes in the composition of the serum, as will be seen from Chapter II. As far as investigated, factors causing the rubber-content of latex to decrease also produce a serum with less solids and a lower specific gravity. The points representing rubber-content and specific gravity in Fig. 1 will therefore deviate from BC in the direction of B'C; in other cases, when there are factors that cause the specific gravity of serum to be increased, points between BC and B''C will be found.

But if the extremes for specific gravity of serum do not differ more than B'' and B' (1.025 and 1.016), the points all fall in a narrow strip on both sides of BC, as will be

Fig. 1.



Specific gravity of latex derived from its rubber-content (in percentage of weight) and the specific gravities of serum and rubber.

clear from Fig. 1; and the relation of specific gravity and rubber-content of pure, undiluted latices is therefore very close.

It is to be remarked that in Fig. 1 the rubber-content is expressed in percentage of weight. When using (as is the general rule, and as is done elsewhere in this book) grams of rubber per 100 cc latex, or lbs per gallon, a recalculation has to be made.

Now the above only holds for pure, original latex. In ordinary practice the latex is mostly diluted to some extent by water, sometimes by a solution of anti-coagulants, and so on; and in determining the specific gravity with densimeters, the latex is often purposely diluted with water, mostly 1:1, to decrease its viscosity and facilitate the reading of the instruments.

By diluting a certain latex with water, the point representing it in Fig. 1 has to be connected with W, representing water with the specific gravity 1.000, and the rubber-content and specific gravity of the mixture may be found graphically or by simple calculation from the mixing-ratio of latex and water.

Thus, diluting a latex O with water 1:1, a point O' will be reached; or diluting latices M and N to a rubber-content of 15 %, the points M' and N' respectively will be reached.

It will be clear that, whilst for pure original latex the relation between specific gravity and rubber-content is pretty close (the small strip along BC), for latices diluted with water there is no simple relation: for latices of between 20 and 45 % rubber-content any point lying in the triangle OWM may be obtained, as the ratio of rubber, serum and water may be. A specific gravity of 0.995 may be found for latices with a rubber-content varying between $23\frac{1}{2}$ % (when undiluted) to $7\frac{1}{2}$ % (when diluted with water from originally 45 % latex). A latex with 20 % rubber-content may show a specific gravity between 0.999 (when undiluted) and 0.9875 (when obtained by dilution from 45 % latex), and so on.

The actual relation between rubber-content and specific gravity of undiluted latices is approximately as follows:

Rubber content (grs per 100 cc.).	Specific gravity.
45 %	0.967 — 0.970
<i>normal</i> { 35 %	0.978 — 0.981
30 %	0.983 — 0.987
20 %	0.997 — 0.998
ca 17 %	1.000

In many places in the older literature specific gravities higher than 1.000 are given for Hevea-latex; it may however be regarded as very probable that these figures all relate to latices other than Hevea (latex from Castilloa or Manihot has a specific gravity higher than water). For Hevea-plantation-latex only in very extreme cases (very low rubber-content of the latex) does the latex reach or surpass a specific gravity of 1.000; for all latices met with in ordinary estate-practice the specific gravity is much lower, as indicated in the table above.

A specific gravity of 1.0002 was stated with certainty in a latex with only 16.0 % rubber-content, obtained after very heavy tapping (two cuts to the wood over the whole circumference, see O. DE VRIES, Arch. 4, Sept. 1920).

An elaborate study of the relation between specific gravity and rubber-content has been made by G. A. VERNET (C. Gp. 1910, page 4549; see also his tables in *Le Latex*, page 475 sqq).

Some of the lowest specific gravities for Hevea-latex, mentioned in literature, are : 0.966 at 26° for a latex containing appr. 48 % of rubber (P. v. ROMBURGH, Med. Pl. 39 (1900), 94), in accordance with the above table; and 0.9555 at 27° 5, mentioned by G. A. VERNET (*Le Latex*, 566) for a latex of unknown rubber-content.

On the use of specific gravity determinations to detect latex of abnormal composition, when it is diluted with water to an unknown extent, see § 61.

§ 16. Viscosity.

Latex is a viscous fluid; the viscosity increases markedly with the rubber-content.

MISS A. T. BORROWMAN (Rubb. Ind. 1911, 243) gave figures for different dilutions of a latex preserved with ammonia, (which preservative in itself, however, decreases the viscosity markedly).

Figures for viscosity of pure undiluted latex are always somewhat uncertain, as latex is not an agreeable fluid for viscosity-determinations, owing to its tendency to clotting and particularly to forming small flakes, which stick in the capillary tube. Undiluted latex, on standing, often shows an apparent increase in viscosity owing to the formation of small clots or flakes; diluted latex diminishes in viscosity on keeping, probably because of the formation of acids and other decomposition products.

Even when using a viscosimeter of the pipette-type, the capillary tube of which is easily cleaned, and adding ammonia (f.i. 1 or 2 percent) to the latex before straining, then variations due the above named errors remain large and the figures are uncertain.

Apart from the rubber-content, the composition of the serum or of the rubber-hydrocarbon might also be expected to affect the viscosity. The differences in viscosity however,

caused by these factors (and calculated on a fixed rubber-content for comparison) are small, and do not lead to the use of viscosity-determinations of latex as a check on the composition of the latex.

H. P. STEVENS (Bull. R. G. A. 2 (1920), 214) mentions very viscous latex, in which instruments as the Metrolac „stick” at almost any reading. This phenomenon, caused by microscopic clots in the latex, seems to be caused by substances extracted from wet bark after rain. STEVENS noted in several cases that the rubber from such latex vulcanised quicker than usual; an explanation of this fact still stands out.

The dimensions of the rubber globules also may play a rôle in the viscosity of the latex: the smaller the globules, the smaller the viscosity is to be expected for a given rubber-content. A difference in this direction was actually found, for instance, latex from young trees showing a lower viscosity; but the direct relationship between viscosity and size of the globules still remains to be determined.

§ 17. Other properties.

In the study of latex other properties have sometimes been used to get an insight into the changes in composition under varying circumstances. Amongst these may be mentioned the depression of the freezing point and the specific electrical conductivity.

An advantage of freezing point determinations is, that relatively small quantities of latex are sufficient, and that small differences in the content of substances causing the osmotic pressure may be detected by it, so that it may do excellent service as a preliminary of further chemical investigations.

E. FICKENDEY (Z. Koll. 8 (1911), 157) used the depression of the freezing point to study the changes in latex after starting tapping (compare § 29).

W. H. ARISZ (Arch. 2 (1918), 357), studying this property, could detect a difference in latex from the roots, the lower and the upper parts of the stem, and used this property to investigate the place of origin of the first and later portions of latex flowing from a cut.

The specific electrical conductivity gives indications as to the dissolved, ionised substances, proteins and other substances which are present in the latex in colloidal solution not affecting it. When the soluble substances are removed by dialysis the conductivity decreases to very low values.

V. HENRI (C. R. 144 (1907), 432; *Le Latex* (1908), 323), in a very diluted latex (containing only 8.7 % rubber) probably preserved with ammonia, found a depression of the freezing point of $0^{\circ}.22$, corresponding with a $\frac{1}{9}$ normal solution of a non-electrolyte or a $\frac{1}{16}$ normal electrolyte-solution. The electrical conductivity was 0.0033 at 25° , corresponding with a 0.25% solution of sodium chloride. By dialysis with water (conductivity 2.10^{-6}) the conductivity of the latex could be diminished to 5.10^{-6} .

§ 18. Changes in latex by physical factors.

Many of the changes in latex, which are of practical importance, will be treated in the next Chapters on the treatment of latex and on coagulation.

It may here be stated clearly that Hevea-latex does not cream on dilution with water or on centrifugation, as is, for instance, the case with *Castilloa*-latex. Statements to the contrary, found here and there in literature, have probably to be ascribed to confusion of Hevea and other latices, or to Hevea-latex in which on standing a certain degree of acidity (and perhaps a beginning of spontaneous coagulation) had developed.

Though the difference in specific gravity between rubber and serum is large enough to allow separation by physical means, the difference in behaviour of Hevea-latex is readily explained, partly by its low resin-content, partly by the smallness of the rubber globules, which in *Castilloa*- or *Ficus*-latex have a larger diameter (0.002 to 0.004. mm.). For experiments on centrifuging, see also § 103.

J. PARKIN (Circ. R. B. G. 1 (1899), 144) stated that Hevea-latex mixes in all proportions with water and shows no tendency to cream, in opposition to what SEELIGMAN asserts (Seeligman, page 102). He further (*ibid* page 142) stated, against BIFFEN's assertion (Ann. Bot. 12 (1898), 168) that Hevea-latex does not cream on centrifugation.

M. K. BAMBER (Circ. R. B. G. 3 (1906), 297) found that in centrifugation even with 11,000 revolutions no separation of rubber and serum is obtained.

H. S. Smith (Lectures 1908, 231) obtained a separation in Hevea-latex by centrifugalisation after addition of acetic acid. See discussion *ibid* page 202.

CL. BEADLE and H. P. STEVENS (Z. Koll. 13 (1913), 210) stated distinctly that creaming is only obtained when centrifugating latex in which aggregates have already been formed.

Freezing also does not alter the state of latex, which on thawing appears to be the same as before, unless the freezing takes too long (compare § 101).

J. PARKIN (Circ. R. B. G. 1 (1899), 145) stated that latex, when frozen to a solid block, melted to practically the same condition as it was before and showed no signs of separation.

B. J. EATON and J. GRANTHAM (J. S. Ch. I. 35 (1916), 722) found that latex can be frozen for a short time and on thawing be reconverted to latex; but when frozen for 4–5 hours, a solid coagulum is found to be formed.

The result of heating latex under different conditions of acidity and dilution is treated in § 100; the changes in latex caused by an electrical current are described in § 194

CHAPTER II.

FACTORS WHICH INFLUENCE THE COMPOSITION OF THE LATEX AND THE PROPERTIES OF THE RUBBER.

In this chapter we will consider which factors have an influence upon the composition of the latex, and what is known of their influence upon the properties of the rubber. In various cases our knowledge is yet very incomplete; but the first condition in coming to know anything is to perceive that it is not yet known.

§ 19. Soil, climate and elevation.

Does the nature of the soil have an influence upon the properties of the rubber? Is latex from a clay soil the same in composition as that from a sandy soil or from marl? And what is the influence of the level of the ground-water, and of the climate? Does rubber from a high-lying estate show properties different from those of rubber from lower regions?

Concerning all these questions little is yet known with certainty. We know very well that these factors can influence the growth of the trees and the *yield* of latex and rubber; but whether the composition of the latex and the properties of the rubber are changed by them, is not yet settled.

It is not easy to collect decisive information concerning such questions. When, for instance, one compares rubber-samples from a number of high-lying estates with others from low-lying estates, one has, at the same time, to reckon with all possible differences in culture, in tapping, and in preparation. Even if one eliminates the last cause of variation by preparing all the samples in a strictly standardized manner, there still remain, as a cause of differences, various factors in planting and tapping which cannot be eliminated, and which, as will be seen from the following paragraphs, may have an appreciable effect.

Since there are no obvious and constantly occurring variations in the properties of rubber from various kinds of soil, climate, and elevation, one may conclude that the influences of these factors, if they exist, are certainly not very great.

At all events these differences are completely concealed by the much greater differences which arise from other causes — treatment of the plot, preparation, etc.

§ 20. Season and weather-conditions.

Something more may be said of the influence of the season. When one taps a certain plot regularly, and carries on the preparation according to a standard method, the fluctuations in the inner qualities of the rubber during the year are small and there is as yet no evidence that rubber, for instance, from the dry monsoon always differs in a certain direction from that from the wet monsoon.

In § 14 we have already mentioned that the rubber-content of pure, original latex is somewhat higher in the dry than in the wet monsoon. The variations in the properties of the rubber may be judged by the following figures for crepe prepared from undiluted latex from one group of trees, variations caused by dilution of latex or method of preparation being carefully excluded (compare also § 67):

Month	Rubber-content	Standard time of cure	Viscosity
May	33.6 %	110	31
June	34.4	112	30 ¹ / ₂
July (dry)	34.5	112	27 ¹ / ₂
August („)	33.0	113	26
September	31.9	110	26
October	32.4	110	27 ¹ / ₂
November (wet)	32.0	106	29
December („)	31.5	107	28

In large and in small groups of trees, from which we always prepared the rubber according to standard methods,

we often found, over long periods, no greater departure from the mean than 5 minutes in time of cure and 3 units in viscosity.

Examples of the uniformity of the product of certain estates during periods of several months or a year are given in § 132 and § 154; in these cases also no pronounced influence of the monsoon was to be detected.

In a long series of experiments made by L. E. CAMPBELL (Bull. Ceyl. No. 27 (1916), 17; Bull. Imp. Inst. 14 (1916), 561), the time of cure of plain unsmoked sheet from two groups of trees, prepared after standard methods, varied from 55 to 80 minutes (average 66.6) and from 67 to 75 minutes (average 71.0) respectively. In the first case the deviations are greater than mentioned above; but in § 153 and 156 we will see that there is more cause of variation in sheet than in crepe.

An influence of the weather-conditions is no more easily detected. A heavy shower after a period of dry weather will, to be sure, cause a noticeably stronger flow of latex, but an influence on the inner qualities of the rubber can not yet be certified.

In actual practice one must of course take into account the fact, that on rainy days the latex, as it comes to the factory, may be diluted by rain. The effect of this factor, which represents an influence on the latex, and not on the trees, is discussed in § 39 and 119.

G. VERNET (Bull. Saigon I (1919), 342) mentions that the latex, after heavy showers, shows a somewhat abnormal relation between rubber-content and specific gravity which only disappears after 8 or 10 days of fine weather. We did not notice this phenomenon in our experiments.

Still one may probably not entirely neglect the climate or the weather-conditions as a source of variability in the product. For instance, we found repeatedly in the dry monsoon, and especially during a long-continued drought, a lower tensile strength than in preceding or in following months; and we are not able to ascribe this deviation to something else than the drought, or the combined influence of wintering and drought.

Further it may be that under conditions other than those in our experiments, for instance in young plots, or on very

poor or dry soil, the influence of the monsoon or of the weather is more pronounced. Reliable data however are still lacking.

It is worth while to mention that the influence of the season is more noticeable when the trees are very severely tapped. The trees are then, as it were, under a great strain, and everything which lessens the strain serves also to change the latex and the rubber and to bring them to a more normal condition (compare § 30 and 32). In such cases the wetter months, with their stronger flow, may differ more from the dry months, in rubber-content of the latex and in rate of cure of the rubber, than they do in ordinarily tapped plots.

For examples see O. DE VRIES, Arch. 2 (1918), 453.

§ 21. Wintering and seed-time.

Beside the changes in external conditions, that cause periodical fluctuations in the growth of the tree and in the flow of latex, but which, as we saw in the foregoing paragraphs, have little influence on the properties of the rubber, the tree in the course of a year also undergoes changes due to internal factors. The most obvious of these are the wintering period and the time of seed-bearing.

Hevea loses all of its leaves once a year, mostly during the dry season; the bare tree in only a few days reproduces a full crown of foliage. The phenomenon of the leaves turning yellow and red, then dropping to the ground, and the tree, after a period of nudity, reappearing in an abundance of young, green leaves, is of course very striking to the planter.

That the wintering may have an influence on the composition of the latex is apparent even to the casual observer on account of a more frequent appearance of violet discolouration on the coagulum during or after wintering. The latex during this period often suddenly shows an increased tendency to discolouration, and though it may be only a few trees which show this phenomenon, one has to reckon with it in estate-practice, for instance, by

using small amounts of bisulphite in the preparation of sheet-rubber (compare § 48 and 136).

That the composition of the latex also shows further changes in connection with this period so eventful for the tree, is apparent from the fact that shortly after wintering the amount of quebrachite may diminish from 2 to 1 %, and that the reducing sugars may disappear for the greater part. The components which have the greatest effect on the properties of the rubber, however, appear to undergo little change; the rate of cure and viscosity of the rubber, prepared according to standard methods, remains practically the same throughout the wintering period (see for instance the figures in § 20).

Whether under other circumstances, such as the wintering of very young trees, the rate of cure and viscosity of the rubber undergo a marked change, remains to be investigated.

An influence of the seed-time on the composition of the latex or the properties of the rubber has not yet been detected.

§ 22. Individual trees.

If one tests the rubber of different trees separately, large differences are found. The values for rate of cure and for viscosity vary from the very lowest to the very highest.

As examples the following figures may be quoted.

1). Good yielders from one estate, all tapped on the same system (two cuts on $\frac{1}{4}$ circumference) and tested at the same time (April 1917):

Tree	1	2	3	4	5	6
Year planted	1907	1910	1907	1908	1908	1907
Dry rubber per diem, in gms, average	35.4	47.8	71.6	23.5	25.6	44.9
Standard time of cure . .	90	<125	>105	120	125	>140
Slope	40	38.5	38	36	37	36
Viscosity	22.2	25.3	30.6	50.6	72.6	90.3

The rate of cure of the rubber from these trees varies from 90 to 140 minutes, the viscosity from 22.2 to 90.6, that is a much wider divergency than in the figures found for ordinary estate-crepe (compare § 132).

See O. DE VRIES, Arch. 4 (1920), 255 and 269.

2). Two 12 year old trees from another plantation, tested during successive months, gave the following figures:

Tree		A			B		
Tapping system		$\frac{2}{7}$			$\frac{1}{5}$		
		Dry rubber, gms. per day	Rate of cure	Viscosity	Dry rubber, gms. per day	Rate of cure	Viscosity
1st month	21.5	105	28	24.5	136	$36\frac{1}{2}$
2nd	"	21.9	115	$24\frac{1}{2}$	—	—	—
3rd	"	24.4	115	28	24.7	140	52
4th	"	22.2	115	31	28.5	137	51
5th	"	26.7	110	30	30.1	131	51
6th	"	9.6	110	$27\frac{1}{2}$	—	—	—

From this example it is seen that the values for rate of cure and viscosity are constant over periods of several months, but differ considerably for the two trees.

For further examples see O. DE VRIES, Arch. 4 (1920), 249 and 268, who found the rubber-content of undiluted latex to vary from 17 to 50 %, the rate of cure of crepe from 90 to 160 minutes, the viscosity from 14 to 90.

When the latex is carefully diluted every day to a standard dilution and the little crepes are prepared in a strictly standardized manner, the viscosity of such samples from day to day is nearly constant. The properties of the rubber, especially its rate of cure, are also generally found constant over a period of several weeks or several months, as in the second table given above. Whether the properties of rubber from a

certain tree remain constant during the course of years, remains to be investigated, as also does the question of how far deviations, such as in the first of the above tables, may be caused by the accidental condition of the tree at the time of testing.

It is worthy of remark that in the first table the tree with the lowest viscosity gives the quickest curing rubber; trees No. 2 and 5, both with a rubber which vulcanizes in 125 minutes, have viscosities of 25.3 and 72.6 respectively. From this it will be clear, that in such cases the viscosity gives no indication as to the properties after vulcanisation.

In West-Java, some years ago, several estates had rubber samples from hundreds of individual trees tested for viscosity, with the idea of using the results in deciding which of the good producers should be used as seed-trees. Such samples, prepared by the estates, are however of no use, because the viscosity for one and the same tree is not constant from day to day, but may show wide variations. As stated above, it is only when the rubber is prepared from the small quantities of latex very strictly according to standard methods, that one secures a fairly constant value for the viscosity from day to day. But the usefulness, even of such exact viscosity determinations, in judging of the properties of the tree as a producer of rubber of good or bad quality, appears, for the reasons given above, to be extremely doubtful.

The composition of rubber from different trees may also vary; data are, however, still scarce.

For analyses of rubber from two trees, prepared by natural coagulation, see Bull. Imp. Inst. 6 (1908), 137. The rubber of one tree contained more ash, more proteid, and more caoutchouc insoluble in chloroform, than that of the other.

§ 23. Strain of seed.

Concerning the influence of the strain of seed on the composition of the latex and the properties of the rubber nothing is known as yet, because all the plantations of *Hevea* from selected seed are still young. In connection with the large

differences, that have been found in the properties of rubber from individual trees (see § 22), one must consider the possibility that such differences are hereditary, and that therefore the strain of seed may give a difference in the properties of the rubber. Due attention is being paid to this question.

§ 24. Age of trees.

This is also a factor, about which it is not easy to collect accurate data. To have absolute certainty, one would have to study one plot of trees during a series of years, during which time all other factors, which may affect the properties of the rubber (tapping system, number of trees per acre, upkeep of plantation, etc.), should remain unchanged. Naturally, such a condition never occurs in actual practice.

From a careful comparison of the figures from a number of plots of different ages it seems clear, however, that the trees, as they grow older, give a rubber which vulcanises somewhat more slowly, and which has a somewhat higher viscosity.

For instance, plots of different age in the Economic Gardens at Buitenzorg gave us the following figures for crepe prepared according to standard methods (latex diluted to 15% rubber-content, crepe rolled next day):

Trees planted in	Age when tested	Tensile strength	Standard time of cure	Slope	Viscosity
1882	35 years	1.29	145	36	50
1898	19 "	1.34	130	37	39
1899	18 "	1.31	135	36 $\frac{1}{2}$	41
1909	8 "	1.26	110	38	28

On an estate, which has a plot of the oldest trees in Java, we found:

Trees planted in	Age when tested	Tensile strength	Standard time of cure	Slope	Viscosity
1889	28 years	1.43	145	36	31
1904	13 "	1.42	135	37	32.5
1911	6 "	1.39	120	36	20.5
1914	3 "	1.41	120	37	24.5

Therefore a decrease is found in rate of cure and an increase in viscosity for trees of greater age; the oldest trees in Java mentioned here give decidedly slower vulcanising rubber than ordinary plots.

For further examples see O. DE VRIES, Arch. 1 (1917), 172 and 176.

In a series of experiments made by L. E. CAMPBELL in Ceylon (Bull. Ceyl. No. 20 (1915), 14; Bull. Imp. Inst. 14 (1916), 561) trees of 16 to 20 years gave on the average a rubber which cured 7% more slowly than trees aged 7 years. The average figures for tensile strength were exactly the same for both groups.

Older divisions from the same estate generally give rubber which vulcanises somewhat more slowly and has a higher viscosity than the rubber from younger divisions, though of course other factors may often obscure this difference. As an example the following figures may serve:

Division	Age in years	Standard time of cure	Viscosity
I	11	>100	37.5
II	8	95	30.5
III	7	95	29
IV	7	>90	28
V	6	80	26

Rubber from very young trees, especially when prepared in the form of sheet, distinctly shows a lower strength when hand-pulled in the unvulcanised state; it is decidedly brittle, and pieces are easily snapped off, even when prepared according to standard methods, so that extreme dilution of the latex does not play a rôle.

In somewhat older plots, of 4—5 years, just taken into the tapping round, the same may often be observed in a lesser degree. This shortness of the raw rubber is not obliterated in the vulcanised product. Rubber from young plots which have just come into tapping has, as a rule, a low tensile strength (1.35 and lower). Besides this it deviates in other properties,

vulcanising quickly (for crepe in 105, for sheet in 85 minutes or less), together with a low viscosity.

As an example of rubber from very young plots, too young to be taken into the ordinary tapping round, but tapped at the base with one cut on $\frac{1}{4}$ circumference by way of experiment, the following figures may be of interest:

	Tensile strength	Standard time of cure	Slope	Viscosity
Mean values for plantation-crepe (comp. § 132)	1.367	115.7	35.8	30.9
Ordinary crepe of an estate; trees 10-12 years old	1.35	122	36	19
Crepe from a plot of trees 3 years old, on same estate.	1.23	81	38.5	11.5
Crepe from a plot of trees $3\frac{1}{2}$ years old, planted at 2500 feet and back in growth.	1.23	60	39	19

From these figures it will be clear that the age of the trees has a certain influence on the properties of the rubber. Rubber from very young trees shows figures which deviate markedly; but the differences between trees of the ordinary tapping age and older ones are not greater than the usual variations in plantation-rubber, and the figures do not seem to lend support to the view that the rubber from old trees is distinctly superior, at least not when trees of 20 or 30 years are compared with 12 or 8 year old trees.

One of the axioms, formulated without being based on accurate data and in which the rubber-culture is still so rich, is that the trees produce a *better* rubber as they grow older. This assertion, however, has been contradicted by various investigators.

E. B. DAVIS (Agric. Bull. Str. F. M. S. 9 (1910), 108, also I. R. J. 39 (1910), 180), from data based on tests from the

Scientific Department of the United States Rubber Co, mentions that the strength of rubber from trees from 4½ to 27 years of age showed very little difference, so that the age of the trees would seem not so important as generally supposed.

G. S. WHITBY (I. R. J. 51 (1916), 790) found the tensile strength of trees 5 years old not less than that of trees aged more than 15 years. See further G. VERNET, Bull. I. Ch. 14 (1911), 791; also C. Gp. 1911, 5503. Further WRIGHT, page 226, where opinions of others are quoted; and the discussion in Rub. Ind. 1911, 258.

With the above mentioned axiom we can only so far agree as to say that young plots, just brought into tapping, often give a rubber with a low tensile strength; but this, after some time, becomes better. We have no reason to assume that rubber from a 12 year old plot, for example, is better than that from an 8 year old one etc.; the lower rate of cure of older plots might even be regarded as a small disadvantage.

In such questions one must not lose sight of the fact that ideas such as the above were often formed in Europe without knowledge of estate conditions. It is perhaps true that older estates often furnish (and especially furnished in former years) better rubber than estates just come into tapping. But one must not forget that preparation on estates, where it has just been started, is (or was) often very imperfect; and also, that young trees give very little latex, so that each bit of water, which remains in the cup or was used for rinsing, dilutes the latex greatly. And so there are other factors capable of causing variation, without the age of the trees having anything to do with it.

Certainly the difference in quality between rubber from young and that from old plots is not so great that the latex would have to be kept separate. On the contrary, when all the latex is mixed, the quantity (generally small) of latex from the youngest divisions does not lower the mean noticeably, and as a result a uniform rubber of normal properties is obtained.

The differences in properties of the rubber caused by the age of the trees now having been discussed, we have to put the question: by which factors in the composition of the latex are these differences caused?

On this point our exact knowledge is still very limited. Even the question as to how greatly the rubber-content of the pure latex is increased as the tree gets older (other conditions, as tapping system and so on, being equal) may not yet be regarded as settled.

CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 216) conclude from a series of experiments that trees four years of age, tapped on the same systems as older trees, give a latex poorer in caoutchouc.

G. S. WHITBY (Ann. Bot. 33 (1919), 314) concluded from a limited number of observations on trees from four to sixteen years old, that the rubber-content in latex increases by 1 to 2% per annum as a tree grows older.

We found however, in the groups of very young trees mentioned above, rubber-contents of 30 and 26%, which would not agree with the above scale.

For latex from young trees the very limited data as yet available point to a composition different from that of latex from trees of the ordinary tapping age.

CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 216) give the following figures for latex of 4 and 10 year old trees:

	Trees 4 year old	Trees 10 year old
Water	70.— %	60.— %
Acetone-extract	1.22 "	1.65 "
Protein	1.47 "	2.03 "
Ash	0.24 "	0.70 "
Sugars in aqueous extract of solids, after inversion (calc. as glucose)	0.21 "	0.12 "

In the composition of rubber, however, derived from young and older trees, no characteristic differences could be stated, at least so far as the ordinary rough separation in groups such as resins, ash and proteins goes.

About the composition of rubber from young and old trees the following data are available.

K. BAMBER (Trop. Agric. Suppl. Vol. I, No. 5 (Nov. 1907), page 100; BROWN, Rubber, page 53) found:

Age of trees in years	2	4	6	8	10—12	30
Moisture in rubber . .	0.70	0.65	0.55	0.85	0.20	0.50%
Ash	0.50	0.30	0.40	0.14	0.22	0.25 „
Resin (acetone-extract). .	3.60	2.72	2.75	2.66	2.26	2.32 „
Protein	4.00	1.75	1.51	1.75	2.97	3.69 „

G. VERNET (Bull. I. Ch. 14 (1911), 792; also C. Gp. 1911, 5503) found the following figures:

Age of trees	5	10	20—30
Ash in dry rubber. .	0.3 %	0.2 %	0.25 %
Resins	1.47	1.44	1.47

In the Imperial Institute the following analyses were made (BROWN, Rubber, page 53):

Age of trees	4 1/2	9	17
Ash in rubber . . .	0.21 %	0.23 %	0.43 %
Resin	2.73 „	2.67 „	1.59 „
Protein	2.88 „	2.89 „	2.52 „

In a number of experiments made by L. E. CAMPBELL (Bull. Ceyl. Nos. 23 and 27; Bull. Imp. Inst. 14 (1916), 561) no difference was found in the average chemical composition of rubber from 7 year old and 16—20 year old trees. The figures were:

Age of trees	7	16—20
Ash	0.225 %	0.256 %
Resin	2.81 „	3.00 „
Protein	2.33 „	2.28 „

The cause of the differences in tensile strength, rate of cure and viscosity, which were treated in the beginning of this paragraph, therefore is not yet determined.

§ 25. Latex from different parts of the tree.

For ordinary estate tapping only the latex of the lower part of the stem is of importance; we will treat the differences from cuts at different heights on the ordinary tapping surface in § 33.

Hevea however gives latex from nearly all parts; from the roots it flows abundantly, and from the branches, young twigs and petioles some latex may also be obtained. Latex from the roots may have some importance in practice, as one of the tricks used by tappers paid on weight of rubber is to dig a hole and profit by the often very rich flow from the roots. The latex vessels in the roots are in direct connection with those in the stem; the latex from the roots, however, has a somewhat different composition, showing a smaller freezing-point depression.

W. H. ARISZ, Arch. 2 (1918), 357.

P. J. BURGESS (Agric. Bull. Str. F. M. S. 3 (1904), 175) gave the following preliminary figures for rubber-content and resin:

	Rubber in latex	Resin in rubber
Large root, below soil-level; small simple cut	43.8%	2.27%
Main trunk, 1—2 ft above the ground, herringbone-tapped	44.4	2.12
Trunk 20 ft above ground, above fork, herringbone-tapped	39.8	1.88

No figures are as yet available on rubber prepared from latex from the roots.

Whether latex from the outer mantles of latex-vessels and the inner ones (near the cambium) is exactly the same in composition, is not determined with certainty; about the rubber obtained from it no data are available.

G. VERNET (J. d'A. T. 10 (1910), 324; Bull. I. Ch. 14 (1911), 335) stated a 3 % higher rubber-content in latex from the deeper layers; W. H. ARISZ (Arch. 2 (1918), 350) found the

rubber-content in deeper layers mostly a little lower, once a little higher, whilst the depression of the freezing-point of latex showed no marked difference.

The latex-vessels in the leaves, petioles and young twigs are not directly connected with the latex-vessels in the stem; the flow of latex from these parts is small, and in practice of no importance. It is however interesting to compare the composition of the latex and the properties of the rubber from these parts with those from the stem. The latex from petioles and leaves seems to show an abnormal composition.

CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 216) found for the dried latex from the drops which exude on snapping the stems of leaves in two:

Acetone-extract	7.12 %
Protein	13.02 „
Ash	1.19 „
Caoutchouc (by difference)	78.67 „
Sugars in aqueous extract, after inversion (calc. as glucose)	2.25 „

The figures for acetone-extract, protein and sugar are much higher than in ordinary latex from the stem, whilst the ash-content is also higher. The authors describe this latex as having, besides a relatively small number of normal rubber globules, smaller globules of about one third of the average size of the rubber globules, and a lower refractive index. They suggest a larger content of resins in these globules (VIII Int. Congr. 25, 581) for which however no direct proof could be given.

No accurate data are available on the rubber from such latex from the younger parts of the tree. The quantity of latex being small, it is not easy to obtain samples large enough for testing, though a comparison with rubber from the stem and rubber from very young trees might be interesting in many respects.

§ 26. Culture.

(Cultivation, Drainage, Inter-planting, Manuring, Thinning)

An influence of these factors on latex and rubber could not yet be stated. It is well known that they may have

an effect on the quantity of latex and thus on the production; but whether such an increase or reduction of the latex-flow also brings with it a change in the composition of the latex, which in turn might cause a change in the properties of the rubber, still remains to be investigated. At all events one may suppose that the influence, if it exists, is not very great; for otherwise some evidence of it would have occasionally been noticed.

§ 27. Diseases.

Concerning the influence of disease, also, nothing is yet known. Leaf-fall disease and brown bast disease may decrease the production; canker may give an increased latex-flow, and it is well known that canker trees may furnish a latex with a very low rubber-content (10 % for example). But whether these influences have an effect on the properties of the rubber, is still unknown.

§ 28. Tapping.

Tapping has a noticeable influence on latex and rubber, which one may summarize as follows: the more strongly one taps the tree, the lower the rubber-content of the latex, and the more quickly the rubber vulcanises. This is coupled with a small decrease in viscosity, whilst tensile strength and slope remain unchanged for ordinary tapping systems, and only begin to deteriorate after very heavy tapping. Everything tending to make conditions easier for the tree produces a change in the opposite direction.

The change in rubber-content is, of course, accompanied by a change in specific gravity, as was discussed in § 15; the figures for rubber-content and specific gravity very nearly follow the line OM in Fig. 1. The points proceed in the direction of M after heavy tapping or other factors which put a heavier stress on the tree, whilst figures in the neighbourhood of O are found, for instance, when starting tapping after a period of rest. Heavy tapping causes the total solids in the serum to decrease somewhat at the same time that the rubber-content decreases markedly,

and a displacement in the direction of M' in Fig. 1 is therefore found.

O. DE VRIES, Arch. 3 (1919), 202.

It may be mentioned here that, though the time of cure of the rubber decreases regularly as the point representing its rubber-content and specific gravity proceeds, for instance, from O to M in Fig. 1, no direct relationship could be traced between different points on OM and the time of cure of the rubber, in such a way that, for instance, a point N should always represent a rubber of, say, 120 minutes cure. The component or components of latex, which cause the differences in rate of cure, are also changed by all the factors which put a heavier stress on the tree; but this change apparently need not in all cases run exactly parallel with the change in rubber-content.

We will now discuss these changes in relation to the various points connected with tapping.

§ 29. Opening a new tapping-cut.

One of the greatest changes in properties, which occurs in rubber, takes place when a tapping-cut is opened after a period of rest. The untapped or rested bark gives on the first tappings a latex with a very high rubber-content (45—50% is entirely normal in this case). Crepe prepared from this latex according to standard procedure vulcanises very slowly, a time of cure of from 150 to 180 minutes being no exception. Externally such latex is often recognisable, sometimes by a yellow colour, sometimes by a strong tendency to violet surface-discolouration.

Now if one continues to tap regularly, the tree furnishes a latex with a steadily decreasing rubber-content. The rubber prepared from it gradually shows a larger rate of cure, while the viscosity decreases, and the slope increases; the tensile strength remains the same.

These changes continue during from 2 to 4 weeks in such a way that at the close of this period an equilibrium has been reached, in which the tree has accustomed itself to the tapping-system. The composition of the latex and the properties of the rubber then fluctuate only within narrow limits. Only the viscosity sometimes increases a

little after the equilibrium in other properties has been reached. What the equilibrium shall be, depends on the tapping system and the condition of the trees.

The decrease in rubber-content of the latex we have already mentioned in § 14; the accompanying changes in properties of latex and rubber may be represented by the following example:

		Original latex		Crepe from 15 % latex		
		Rubber-content %	Specific gravity	Standard time of cure	Slope	Viscosity
	2nd day	44.0	0.9689	145	32½	20½
	3rd "	39.4	0.9708	145	32½	23½
	6th "	35.0	0.9769	140	34	20½
	9th "	33.8	0.9784	135	34½	18½
	13th "	30.4	0.9831	125	35½	18½
	16th "	29.6	0.9853	115	35	16½
	20th "	28.0	0.9878	107	35½	18½
	25th "	26.4	0.9902	103	36½	18½
Equilibrium	5th week					
	(average)	25.3	0.9914	99	36½	18½
	6th week					
	(average)	24.6	0.9921	96	37½	20
	7th week					
	(average)	25.7	0.9915	98	37½	20

The trees were tapped with two cuts on ¼ circumference.

The latex was in this case diluted to 15 % rubber-content and the coagulum rolled to crepe the day after coagulation; when crepe is prepared from undiluted latex, the difference in time of cure is not so great, as will be discussed in § 67. For further details see O. DE VRIES, Arch. 2 (1918), 248. For other examples see O. DE VRIES, Arch. 1 (1917), 287; 2 (1918), 453; 3 (1919), 126, 200 and 202, where during the first days the crepe from 15 % latex showed a still lower rate of cure, the figures being 180, 160, 170, 155 minutes.

Still larger differences may be found when using heavy tapping systems, for which the state of equilibrium lies still further from the original status of the untapped tree

(see § 32). For instance, when tapping with two cuts on the whole circumference the following results were obtained.

	At the opening of the tapping cut	After the state of equilibrium is reached
Rubber content of latex. . .	40.6 %	19.3 %
Specific gravity of undiluted latex	0.9710	0.9972
Standard time of cure of crepe from 15 % latex	155	95
Viscosity of same.	35	25

See O. DE VRIES, Arch. 3 (1919), 201 and 202.

The composition of latex and rubber also show marked changes on continued tapping after the trees had a period of rest. When using a heavy tapping system the following figures may be found for the composition of the latex:

D A Y	1	3	12	18	22	33
Rubber-content of latex.	43.0	39.3	31.5	25.8	21.8	14.8
Total solids in latex. .	45.1	42.1	34.7	29.2	24.8	17.3
Nitrogen " " . . .	0.28	0.29	0.29	0.24	0.23	0.18
id. in % of total solids	0.61	0.68	0.78	0.81	0.92	1.06
Ash in latex. . .	0.60	0.72	0.61	0.63	0.75	0.77
id. in % of total solids	1.34	1.72	1.77	2.17	3.02	4.47

The rubber-content decreases, and the ash in latex and in total solids increases in the same way as above. The nitrogen is nearly constant when calculated on the latex, and therefore increases as percentage of the total solids.

W. H. ARISZ, Arch. 4 (1920), 31.

The composition of the serum also changes; the total solids and at the same time the specific gravity decrease, but the inorganic matter increases somewhat. For the above given example of tapping with two cuts on the whole circumference the figures are:

	At the opening of the tapping-cut.	After the state of equilibrium is reached.
Specific gravity of (original) serum.	1.0195	1.0173
Total solids in original serum (calc. on serum)	4.84 %	3.87 %
Ash in original serum (calc. on serum). . .	0.59 %	0.81 %
Ratio of ash to total solids.	1 : 8.2 (12.2 %)	1 : 4.77 (20.9 %)

O. DE VRIES, Arch. 3 (1919), 201 and 202.

The composition of the rubber shows the following changes:

Day after opening the tapping-cut	5	12	18	30	47
<i>Crepe from undiluted latex,</i>					
ash	0.27	0.32	0.40	0.39 ⁵	0.39
nitrogen	0.34	0.40	—	0.57	—
acetone-extract	2.8 ⁵	3.0 ⁵	2.9	2.8	2.7 ⁵
<i>Crepe from 15 % latex,</i>					
ash	0.14	0.20	0.21	0.27	0.27
nitrogen	0.26	0.37	0.45	0.54	0.55
acetone-extract	3.0	2.6	2.9	2.9	2.4

The ash in rubber increases on continued tapping, the acetone-extract remains constant. It is especially interesting to note that the nitrogen-content of rubber increases, whilst the nitrogen-content of latex decreases.

See O. DE VRIES, Arch. 4 (1920), A 313.

The decrease in rubber-content after opening a tapping-cut has been noted by many authors; see especially G. VERNET, Bull. I. Ch. 8 (1905), 720. In many cases no special measures were taken that the figures relate to pure, original latex, and conclusions are not possible as dilution or evaporation may have played an unknown role.

We have already mentioned in § 14 that for individual trees the difference between the rubber-content after beginning tapping, and at the state of equilibrium, may not be so large as in the above example.

G. VERNET (*Le Latex*, 565) gave figures for the increase in specific gravity, which accompanies the change in rubber-content. He mentions (*Bull. Mars.* 1 (1919), 117) that in the beginning of tapping the sugar-content of latex may be 3%; it decreases on continued tapping.

W. R. TROMP DE HAAS (*Ann. J. Bot.* 3me Suppl. I (1910), 443), on continued tapping on alternate days with different heavy systems then in use, found the ash and the nitrogen in the total solids in latex to increase, but the figures were somewhat irregular. In another experiment (*Teysm.* 13 (1902), 265) the same author found the nitrogen-content of latex to decrease from 0.364% on the first to 0.273 on the seventh tapping, using the alternate day system.

R. H. LOCK and M. K. BAMBER (*Circ. R. B. G.* 5 (1910), 73, 209 and 231), for tapping systems with intervals from 1 to 7 days, found the rubber-content of latex (not always pure and undiluted) to diminish, after tapping was begun, from 40–50% to 30%. The resin-content of the rubber was found to fall off with continued tapping, and this slightly more in cases of frequent tapping; the ash showing no difference. The „organic matter, chiefly proteids” for frequent tapping decreased at first to 0.8%, then increased again to 1.5%; for tapping intervals of five, six or seven days it steadily decreased from 1% to 0.7%. The „breaking strain” showed no appreciable change with continued tapping.

E. FICKENDEY (*Z. Koll.* 8 (1911), 157) followed the change after starting tapping with a view to studying the so-called wound-response. In tapping at intervals of two days or more for a period of one month, he found that the total solids in latex diminished from 51.74 to 42.85% and from 49.8 to 39.2%, whilst the ash remained constant (appr. 0.42%) and the depression of the freezing-point first diminished, then increased again. This indicates that the molecular concentration of dissolved substances, which cause the osmotic pressure, changes in the same way.

The marked change in properties of the rubber after opening a tapping-cut on trees that have had a period of rest may be important as a cause of variability in the product of estates, for instance, when tapping is stopped for a month or more during and after the period of wintering. The rubber, obtained during the first days or weeks after tapping is resumed, will cure more slowly than the usual

product of the estate, and unless special measures are taken, the rubber from the first days of tapping may take an abnormally long time to cure.

One of the precautions to be taken would be to prepare crepe from pure, undiluted latex, instead of sheet or crepe from 15 % latex, as we will show in § 67. Another measure would be to mature to some extent the rubber secured during the first days, so as to increase its rate of cure; but such a procedure would be rather too complicated for ordinary estate-practice.

§ 30. Periods of rest; tapping-intervals.

If we interrupt tapping by a longer or shorter rest period the contrary, as it were, of what we discussed in the foregoing paragraph takes place. The tree repairs itself, and when we start tapping again, the latex has a higher rubber-content, and the rubber vulcanises more slowly and has a higher viscosity. When regular tapping is again begun after a short period of rest, the former equilibrium is often quickly reached again, and the deviation is often negligible.

The effect of a rest is more marked when the tree is heavily tapped, and thereby under a certain strain. Every factor tending to relieve the strain causes latex and rubber to return to a more normal state. The following are figures for the state of equilibrium for trees tapped with two cuts on $\frac{3}{4}$ circumference, and further for the first days after a rainy period, during which tapping had to be stopped for 7 days out of 14:

	Latex		Crepe from 15% latex	
	Rubber-content	Specific gravity	Standard time of cure	Viscosity
Average before rainy period	16.9	0.9964	106	28
1st day after period of interruptions . .	20.5	0.9950	—	—
2nd day after period of interruptions . .	16.8	0.9959	122	41 $\frac{1}{2}$
3rd day after period of interruptions . .	86.3	0.9962	122	39

For these same reasons, trees tapped every other day furnish a latex with a somewhat higher rubber-content than is secured by daily tapping. Whether the properties of the rubber in this case are also changed in the sense discussed above remains to be seen.

J. C. WILLIS and M. K. BAMBER (*Trop. Agric.* 29 (1907), 246) regarded it as fairly certain that when using a longer interval than two days, the latex gets richer in rubber and produces a better quality of rubber. The experimental material to base on was, however, very scarce.

R. H. LOCK and M. K. BAMBER (*Circ. R. B. G.* 5 (1911), 209; *Bull. Ceyl. No. 1* (1912), 19) compared latex and rubber from trees tapped with three V's on $\frac{1}{2}$ circumference with the Bowman-Northway knife, followed by a pricker, with intervals from one to seven days. The rubber-content of latex (which however was not always pure, original latex when tested) varied from 30 to 40 % with the increase in length of intervals. The rubber, when tapped after longer intervals, showed a somewhat larger resin-content and markedly less „organic matter, chiefly protein” (method of determination not described), whilst the ash remained the same and the „breaking strain” (of which however no definition is given) decreased somewhat.

M. K. BAMBER (*Trop. Agric.* 49 (1917), 324), for tapping daily or on alternate days with one cut on $\frac{1}{3}$ circumference, gives, as the average over a period of three years, 29.1 and 32.0 % rubber in the latex, which however was not collected with all precautions to obtain it in the pure, undiluted state.

In experiments conducted at Ceylon (see summary by T. PETCH, *Bull. Ceyl. No. 42* (1919), 6) the rubber-content of the latex (which however was not always the unchanged original latex) on the average was 30.2 % for tapping three times a week, 38.2 % for tapping twice, and 41.3 % for tapping once a week.

G. VERNET (*Bull. Mars. 1* (1919), 177) mentions that a short rest or an interruption of tapping may cause an increase in sugar-content of latex and make spontaneous coagulation easier.

The chemical composition of biscuits obtained from groups of trees tapped with intervals of 1 to 7 days was investigated by the IMPERIAL INSTITUTE (*Bull. Imp. Inst.* 11 (1913), 375). In resin and ash no difference was found; the protein-content was somewhat lower with longer tapping intervals, but the differences were not very pronounced.

§ 31. Deep and shallow tapping.

Shallow (undeepest) tapping may also have the same effect as rest: the rubber-content of the latex increases, the rubber itself vulcanising somewhat more slowly with a

higher viscosity. This is very noticeable when one taps heavily, and each lighter tapping makes a great difference for the tree. Whether, or not, with the ordinary mild tapping-systems, deep or shallow tapping has a similar influence in actual estate-practice, is not yet determined; but presumably the variations in such a case will be insignificant.

As an example of the combined influence of a short rest and a lighter tapping, the following figures may serve for trees tapped daily with two cuts on $\frac{1}{2}$ circumference. The state of equilibrium was:

	Original latex		Crepe from 15% latex	
	Rubber-content	Specific gravity	Standard time of cure	Viscosity
	24.4 ⁵	0.9916	111	34

Due to the illness of the tapper the trees then had a rest of 5 days; the new tapper tapped very carefully at first, and only gradually got to the usual depth. The figures show a marked difference with the above, and were:

1st day	26.3	0.9885	120	42 $\frac{1}{2}$
2nd "	28.3	0.9873	> 115	41
5th "	27.7	0.9874	120	41
6th "	27.5	0.9879	125	38
7th "	29.3	0.9877	130	41 $\frac{1}{2}$
2nd — 3rd week	26.6	0.9899	116	42 $\frac{1}{2}$

O. DE VRIES, Arch. 2 (1918), 444 and 453.

The increase in rubber-content and the change in rate of cure and viscosity, as discussed above, are very marked in this case of rather severe tapping.

Some data on the chemical composition of rubber (crepe) obtained by different tapping instruments (knife and pricker) are mentioned in Bull. Imp. Inst. 10 (1912), 380. A marked influence of the tapping system on the composition of the rubber could not be found.

§ 32. Length and number of tapping-cuts.

Heavy tapping gives the results discussed above: lower rubber-content, more quickly curing rubber, sometimes also a lower viscosity. For the tapping-systems now generally in use the differences are however not very great, falling

as they do within the limits of variation for ordinary estate-rubber.

The following data will serve as an example.

Experi- ment	Description	Rubber- content of latex	Specific gravity of 15% latex	Stand- ard time of cure	Viscosity
I.	one cut over $\frac{1}{3}$ circumference	24.2 %	0.9926	> 95	33 $\frac{1}{2}$
	" " $\frac{1}{4}$ "	26.2	0.9920	< 100	34
	" " $\frac{1}{5}$ "	27.3	0.9918	100	30 $\frac{1}{2}$
	" " $\frac{1}{6}$ "	26.3	0.9917	< 105	30
II.	Three cuts over $\frac{1}{4}$ circumference	24.2	0.9932	< 95	35 $\frac{1}{2}$
	Two " $\frac{1}{4}$ "	26.9	0.9929	< 100	35
	One cut $\frac{1}{4}$ "	28.6	0.9920	105	33

O. DE VRIES, Arch. 4, Sept. 1920.

Although the variations are relatively small, yet it will be seen that the tapping-system may offer the explanation for a part of the variations in properties of the rubber from different estates.

Heavier tapping-systems give greater deviations. As an example the following figures may serve for groups of trees from one field:

1	2	3	4	5	6	7
	Tapping-system					
	1 cut on $\frac{1}{3}$	2 cuts on $\frac{1}{4}$	2 cuts on $\frac{1}{4}$	2 cuts on $\frac{1}{2}$	2 cuts on $\frac{3}{4}$	2 cuts on $\frac{1}{1}$
<i>Original latex</i>						
rubber-content (see § 14)	33.6 ⁵	31.2	29.1 ⁵	26.6	22.6	22.2 ⁵
specific gravity	0.9823 ⁵	0.9849	0.9876	0.9902 ⁵	0.9942 ⁵	0.9945
<i>Original serum</i> (calc. from acetic acid serum)						
specific gravity	1.0226	1.0223	1.0219	1.0207	1.0188	1.0189 ⁵
total solids in serum (grams per 100 cc. orig. serum)	5.27	5.20	4.95	4.57	4.09	4.13
ash in serum (id.) . . .	0.74	0.79 ⁵	0.77	0.86	0.82	0.86
ash in % of total solids in serum	14.0	15.2	15.5	18.8	20.1	20.8
<i>Crepe from 15 % latex</i>						
tensile strength	1.39	1.36	1.36	1.40	1.36	1.35
standard time of cure .	130	112	118	110	102 ⁵	101
slope	36 $\frac{1}{2}$	36 $\frac{1}{2}$	36 $\frac{1}{2}$	37	38	38 $\frac{1}{2}$
viscosity	34	31 $\frac{1}{2}$	29	31	29	34
ash	0.16	0.16	0.17	0.21	0.26	0.26

O. DE VRIES, Arch. 3 (1919), 199 and 202; *ibid.* 4 (1920), A 315, further Arch. 1 (1917), 277 and 288.

The differences are marked, covering nearly the whole range of variation in ordinary estate-crepe. At the same time from the difference between columns 3 and 4 it is clear that it is not only the tapping-system that determines the composition of latex and rubber, but that the „condition of the trees” (to conceal the still unknown factors under this name) may also be of importance.

By very severe treatment of the trees, such as tapping to the wood, without sparing the cambium, with one or two cuts on the whole circumference, we could get still further deviating figures, namely:

rubber-content of original latex	16.0 %
specific gravity	1.0001
standard time of cure for crepe from 15 % latex	90

As mentioned in § 14, W. BOBILIOFF by special methods (tapping of insulated pieces of bark) obtained latex of 4 — 10 % rubber-content. Neither this latex nor the rubber from it have as yet been investigated, the quantities being only small. However, with such a low rubber-content a specific gravity of latex higher than 1.000 is to be expected.

CL. BEADLE and H. P. STEVENS (*I. R. J.* 41 (1911), 216) found the rubber-content in pure latex to differ from 43 to 18.5 % with different tapping systems, some of them heavy, as used in former years.

§ 33. Height of tapping-cut on the stem.

The trees are usually tapped only on the lowest part of the trunk, which is easily within reach, and which contains the largest number of latex vessels. The tapping-area is generally confined to a height of 1 or at the most 1½ Metre from the ground, and it is only when no tappable bark in that area is available, that higher tapping is resorted to.

Whether one taps higher or lower in the usual tapping area, and whether one takes latex from the upper or the lower cut, where two cuts are used, makes little difference so far as latex and rubber are concerned.

The lower cut, to be sure, yields more than the upper one, and this difference appears to increase as the tapping-surface is used up, and the upper cut thus left on a narrower piece of bark between two tapped areas.

This difference in yield, however, does not seem to be accompanied by a difference in composition of the latex or in the properties of the rubber: the differences in latex and rubber from upper and lower cut, collected separately, were found to be insignificant.

O. DE VRIES, Arch. 1 (1917), 283 and 288; Arch. 3 (1919), 128. We have already mentioned in § 12 that the tendency to oxydation generally increases, the higher the cut is placed on the stem. A small difference in this direction may often be detected between the ordinary upper and lower cuts.

What the properties of rubber and latex from higher regions are, for example above the ordinary tapping area and still higher, has not yet been investigated.

W. H. ARISZ, (Arch. 2 (1918), 357) found the latex from higher cuts to show a larger depression of the freezing-point than that from the ordinary tapping height.

§ 34. Early and late tapping.

The hour at which tapping is done, may have an influence on the latex-flow. Earlier tapping often gives more latex, but this depends on the climate (cloudiness, sunshine, temperature, etc.), so that a rule for all estates can not be given.

See H. VAN LENNEP, Arch. 3 (1919), A 80.

Tapping at a later hour may give a latex with a higher rubber-content. Whether this is simply due to evaporation in the cup, which must be greater in the hot hours of the day, or whether the latex already shows a higher rubber-content as it exudes from the tree, is still unknown.

A. E. COLLINS (I. R. J. 43 (1912), 99) found the latex, that usually contained 35% of dry rubber, to yield 63.6 and 61.7% when tapping was postponed till 9 a.m. and the sun already high up.

Compare also O. DE VRIES, Arch. 4, Sept. 1920.

So far as investigated up till the present, early or late tapping, although it has an effect on the yield of latex, gives very little difference in composition of latex and in the properties of the rubber.

See O. DE VRIES, Arch. 4, Sept. 1920.

§ 35. Changing the tapping-surface.

When a tapping-surface has been used up, tapping is changed over to another section of the tree, which is then regularly cut from above downward. A change of tapping-surface therefore means starting tapping in bark that has had at least partial rest; and further a displacement of the tapping-cut from the lowest to higher regions. This change may be visible in the colour of the latex, showing either a yellow or a tendency to violet discolouration, which phenomena, as we saw in § 29, often appear on opening a tapping-cut on trees that have had a period of rest. At other times nothing is to be seen from the latex.

With the further composition of the latex and the properties of the rubber it is the same; at times the change to a new tapping-surface having no effect, at other times a slight one. This question deserves further study; but one can easily imagine that in some cases the newly tapped bark was affected by the former tapping, and in other cases not. The large deviations in properties of the rubber, notably the slow rate of cure, that is found when opening a tapping-cut (see § 29) does not, however, appear when changing to a new section of bark on trees tapped regularly.

When at the time of changing over the tapping-surface a new tapping-system also is adopted, more opportunity, of course, is given for a change in latex and rubber, which, according to whether the new tapping-system is more or less severe than the old, will be as pointed out for such cases in § 30 and 32.

In different cases a variation of from 5 to 15 minutes in time of cure, and of from 4 to 10 units in viscosity, were found.

As a rule, now-a-days, tapping-systems differ so little in total length of tapping-cut, that in estate-practice presumably no important deviation in the properties of the rubber will arise through the change to a new tapping-surface. This is still further helped by the fact that on most estates the tapping-surface is not changed on all the trees on the same day, but takes place gradually when the old tapping surface on each tree is used up.

§ 36. Topping (pollarding) the trees.

When the trees grow older, the space between them is filled up with branches and gradually becomes insufficient, so that trees have to be felled to make room for their neighbours. On some estates the trees to be thinned out are at once felled and taken away, but on others they are first topped (pollarded) at a height of 3—4 M. and the stumps are then used, either as a tapping-school to train the tappers, or as rubber-producers.

After pollarding the latex-flow decreases rapidly, and the yield falls greatly; but it may take months, and sometimes even years, before the latex-flow completely ceases.

Pollarding affects the latex in the same way as a „heavier stress”: the rubber-content falls off, the rubber vulcanises somewhat more rapidly and shows a smaller viscosity, while the tensile strength appears to be unaltered, or perhaps sometimes shows only a small decrease. The differences are however of no practical significance. The following are mean values found in an experiment during a period of four weeks before and four weeks after the pollarding of the trees.

	Before topping	After topping
Rubber-content of original latex	25.8 %	21.1 %
Specific gravity of original latex	0.9912	0.9955
Standard time of cure of crepe from 15 % latex	100	90
Viscosity of crepe from 15 % latex	21	18

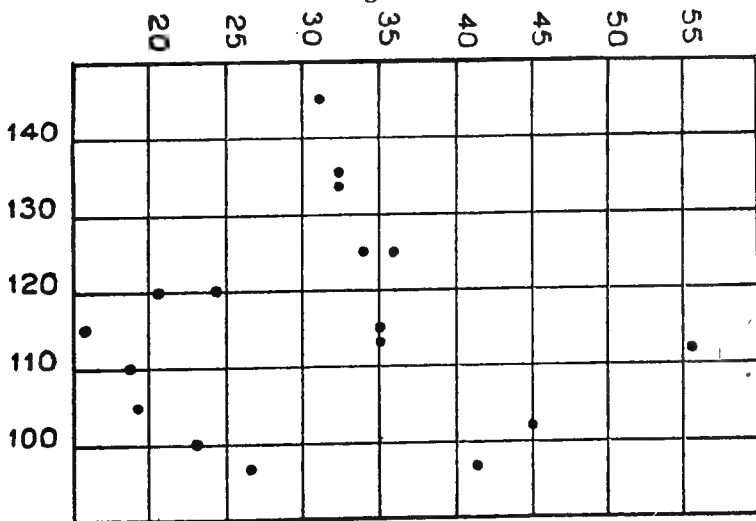
It follows that one can safely mix the latex and rubber

from pollarded trees with the ordinary estate-product, without fear that the product will deteriorate because of this mixing.

§ 37. Summary; the mixing tank.

In reviewing the points discussed in this chapter it will be clear, that there are a number of factors which cause changes in the latex and consequently in the rubber. Very great variations appear in the properties of the rubber secured in the first week after the opening of a tapping-cut, before the state of equilibrium is reached. Heavy tapping can also give important deviations. This latter factor, however, now-a-days seldom appears in ordinary estate-practice and only in special cases will be a cause of variability in the product. A change of tapping-surface or of tapping-system, even in the systems most commonly used at present, may cause deviations; and more important still in many cases is the age of the tree, especially when starting tapping in young plots. And as we have seen in the foregoing paragraphs, there are still other, and perhaps also still unknown, factors, that may cause variability in the product.

Fig. 2.



Standard time of cure and viscosity of a number of samples, prepared in strictly the same way, but from latices of different origin; showing the variability caused in the properties of the rubber by differences in composition of the latex.

It is therefore not to be wondered at that one can detect great differences in properties of the rubber, even when it is prepared in strictly the same manner. In Fig. 2 the values for time of cure and viscosity are given for a number of samples which we prepared ourselves on different estates, always in exactly the same way, either from the mixed latex or from the latex of certain divisions or fields separately.

The latex was always diluted to 15 % rubber-content and coagulated with acetic acid, without addition of other chemicals; the coagulum was creped the day after coagulation.

We purposely mention no such experiments with smoked sheet, because the drying and smoking are so difficult to standardize (see Chapter X).

It will be seen from Fig. 2 that, even in the relatively small number of samples reproduced in it, the time of cure varies from 95 to 145 minutes, while the viscosity varies from 16 to $55\frac{1}{2}$. These are nearly the highest and the lowest values to be found in ordinary estate-crepe (see § 132, 203 and Chapter XX). Still more abnormal times of cure might be obtained just after opening a tapping-cut, in which case values such as 170 and 180 minutes may occur.

The „composition of the latex” therefore may cause as great a variation in the rubber as the „preparation”, if not a greater one; and in proportion as the preparation on estates becomes more and more standardized, variations in the latex will be of more and more importance as a cause of variability in the product, because they depend on the condition and the treatment of the plantation, which can not always be regulated at will.

For the present the only method, and it is at the same time a highly satisfactory one, of neutralizing the differences in latex is: the mixing of as large quantities of latex as possible. By this procedure the differences in rubber for a given estate are completely removed, whilst the estates individually also come nearer the general mean values. We will come back to this subject in § 53.

The possibility remains that a method of preparation may be discovered, which will eliminate or take away the differences

in the latex. So long, however, as we know so very little about the serum-constituents, we grope in the dark. In the description of patented processes the claim is often put forward with emphasis, that they give an unusually uniform rubber; but up to the present no process of preparation is known with certainty, which in this respect gives more satisfactory results than the ordinary, well-conducted standard preparation.

CHAPTER III.

COLLECTION OF THE LATEX AND THE USE OF CHEMICALS.

§ 38. The latex in the field.

The latex in the field is exposed to various dangers, but the influence of these upon the rubber is more suspected than known.

That dirt (leaves, bark-scales, grains of earth etc.), falling into the cups or pails, is a serious detriment, is obvious, since only a part of it is removed by straining.

Bacterial contamination, also, is in many cases decidedly injurious, and some sorts of spots on the rubber owe their origin to this. Formation of lump appears, in certain cases (for example dirty spouts), to be promoted by such contamination.

An example where lump-formation and curdling were much diminished by the use of clean spouts, is given by J. C. HARTJENS (*Arch.* 2 (1918), 170).

Yet our actual knowledge on these points is still very incomplete. For example the causes of lump-formation and of premature clotting, or curdling, are far from explained.

Concerning the effect of direct sunlight on the latex, very little is positively known. Most experts agree that direct sunlight had better be avoided; but how far one must go in this, and what the consequences are, is not yet determined. Presumably the principal point is that the latex gets warm; and that this may promote spontaneous coagulation and lump-formation by evaporation. That sunning the latex will affect the properties of the rubber prepared from it, as it affects the dry rubber (see § 164), has not yet been shown.

To keep the latex cool and retard the growth of bacteria causing spontaneous coagulation, it is sometimes advisable

to use white utensils (pails etc.) and not dark ones; and to wrap the pails or cans in pieces of wet cloth. Data on the effect of such measures are however not available.

The properties of rubber from partial coagulation and of lump, about which more is known than as to the manner in which they are formed, will be discussed in § 176 and 177.

§ 39. Dilution of latex in the field.

Latex may be diluted in the field in several ways, and the chances of this are so great that it requires special care and control to get undiluted, or nearly undiluted, latex to the factory.

In former years it was the custom to paint the freshly opened tapping-cut with water, to facilitate the flow of latex; the volume of water so added often appreciably exceeding the volume of latex. Further, when collecting the latex, it was sometimes washed down the cut with some water. The coolies, in addition to the pail for collecting the latex, had to carry another pail with water, supposed to be clean water from the factory, but which may often have been replaced by dirty water from a streamlet or drain nearer the trees and in this way more convenient. Though it was quite natural to aid the thick latex in flowing down to the cup, early experiments soon proved that the yield was rather decreased than increased by this practice, and it has long since been completely dropped.

On the use of driptins, from which a small amount of water is constantly kept running on the cut to make the flow of latex easier, see P. ARENS (Arch. 3 (1919), 42), who found no increase in yield with this system.

The idea that the latex should be diluted as soon as possible, to restrict lump-formation, has however not yet been given up by all planters, and has never been sufficiently disproved. The opinions of different investigators are not in agreement on the question as to whether or not the use of water in the field promotes formation of lump; and though several of them have argued that the percentage of lump is less when collecting the latex undiluted in dry

cups, definite proof and figures for different circumstances (for instance, dry and wet monsoon) have not yet been given. A number of estates still place a small quantity of water in the cup, or allow the wall of the cup to be wet, to avoid drying up of the latex by evaporation.

This „small quantity” of water may however dilute the small quantity of latex, given by one tree, considerably, especially when the tree is a bad yielder. Sometimes not water, but a solution of anti-coagulant is placed in the cup; but to be certain that every cup gets its proportionate part is rather difficult, and most estates prefer to add the anti-coagulant, if necessary, in the pails. It can then be distributed in the pails at the roll-call in the early morning, before the coolies start to their tapping task.

A third occasion of adding water occurs in the process of pouring the latex from the cup into the pail. Thick, viscous, undiluted latex of course sticks to the cup, and too much latex—or too much time—would be lost in letting it drip out of itself. It is therefore wiped out with some kind of instrument, of which the most natural is the coolies finger. Many estates allow a „wet finger”, with which the latex is more easily removed; that is to say, the coolies carry a pail of water, in which the cup is washed after the latex has been collected, and the hand, wet from washing the cup, is used to wipe the latex of the following cup into the pail. As it is hard for a coolie to believe that an increase in volume will not help to increase the pay, it is difficult to keep this wet finger rather dry, especially when coolies are paid, not by task but by the amount of rubber collected.

A fourth source of dilution is the intentional addition of water to the latex by coolies aiming at an increase in weight. This addition is made where it may most easily be done without detection, and not where the water is cleanest.

Further it is rather difficult, as we stated in § 14, to have the cups really dry. Aluminium cups, which are daily brought to the factory to be cleaned, are generally placed one inside the other, and a large amount of water sticks between the cups. Glass cups, which remain in the field, may remain

wet from washing or become wet from rain in the afternoon or night, especially when they are kept right side up. Only the so-called „dry wash” gives sufficient guarantee of undiluted latex: after collecting, the remaining latex is left in the cup and soon dries to a film, the cup being hung upside down on a pole or on a wire hook on the tree; the next morning the film being collected and used to rub the cup clean on the inside (see also § 180).

The sources of dilution of the latex are therefore many; and it should not be forgotten that many planters are not averse to it, because dilute latex passes the sieves so much more easily and quickly than the thick, viscous undiluted latex, and gives no clotting on or in the holes of the sieve.

That the use of dirty, muddy water from streamlets or from the drains must be prevented at any cost, will be acknowledged by every one. In the first place even relatively small quantities of the silt or fine clay-suspension in coloured water, which on standing gives no deposit, may injure the colour of the crepe and produce a grayish, yellowish or even an orange-coloured product. Further the fine particles of soil may pass the sieves and only partly settle before the latex, after the addition of acetic acid, gets so viscous that no further separation is possible; so that a part of them gets into the coagulum. When once the latex is allowed to come to the factory in a somewhat diluted state, it is very difficult in practice to get the coolies to carry, and use, only clean water and to prevent the addition of dirty water in the field. This consideration alone should inspire every one to aim at the collection of pure undiluted latex.

We have several times tested rubber from different sources that showed an abnormally low tensile strength along with other properties which were normal, the viscosity especially being normal. Though positive proof could not be obtained (in the ash nothing abnormal could be found by microscopic examination) a mechanical admixture of dirt of some kind was suspected as the cause of the low tensile strength (see also § 119). The point, however, needs further clearing up, as fine powders such as gypsum or talcum, when added to the rubber in small quantities, do not affect the tensile strength, so that there is no reason to suspect such an affect, at least from the very fine silt in water.

§ 40. Dilution with water of abnormal composition.

In special cases abnormal phenomena may be caused by diluting the latex. So on the calcareous soils in some districts of Java the water may cause premature coagulation. When water is added to the latex in the field, for instance when rinsing the cups, this results in an abnormally high percentage of lump. The effect is still more striking when such water is used to bring the latex to standard dilution: an immediate curdling may be produced, and soon the whole latex clots, so that the further handling presents great difficulties, and it can no more be worked into sheet. The high content of calcium-salts (and perhaps other salts also) may be regarded as responsible for this effect.

J. C. HARTJENS, Arch. 2 (1918), 184.

Another case of abnormal effects is presented by the slightly acid water of some springs in volcanic districts. Such water also may cause rapid curdling or clotting of the latex, and is unsuitable for use in rubber preparation. That a strongly acid volcanic water can even be used (though not recommended) as a coagulant, will be treated in § 91.

For estates in the neighbourhood of the sea the influence of brackish water may be of interest. The effect of using it for diluting the latex is to retard the rate of drying, which in the preparation of sheet may become very troublesome. The rate of cure decreases markedly, and the viscosity somewhat.

Common salt (NaCl), when used in large quantities, is a coagulant (see § 90); the effect of the chlorides and carbonates of magnesium and calcium deserves further investigation.

§ 41. Anti-coagulants.

Latex is not a stable fluid; on the contrary it has a decided tendency to curdle or to form clots, as was shown in the foregoing paragraphs. The different factors which may cause clotting or lumping will be discussed further in § 177. Curdling and clotting, of course, means a loss to the planter, as the rubber produced from what remains on the

sieves is more or less brown, and brings a lower price than the first grade. To avoid premature coagulation, solutions of anti-coagulants are added to the latex when necessary. A small amount of these may be placed in the cups in which the latex drips from the tapping-cut, or they may be placed in the collecting pails and so become mixed with the latex as the coolie pours in the contents of his cups. Again they may be added to the latex when it arrives at the factory, thus preventing coagulation during the time the latex of coolies coming to the factory is received, measured, strained and mixed prior to coagulation.

The effect of anti-coagulants in preventing premature coagulation may be:

1) purely chemical, i.e. they neutralise the acid which may be formed spontaneously in the latex, and so retard coagulation; or they render inert certain substances which promote coagulation (for example, by precipitating calciumsalts);

2) disinfecting or poisonous, that is, they hinder the growth of the organisms, or paralyse the enzymes which cause coagulation.

We mentioned in the foregoing paragraphs that there are many things about premature coagulation which are not yet explained; and this is also true of the effect of anti-coagulants. As to which anti-coagulant is best under different conditions, opinions still vary.

During coagulation a part of the anti-coagulant (whether changed or not by the acid used for coagulation) is absorbed by the coagulum and may in this way have an influence upon the properties of the rubber. At the same time the anti-coagulant, which generally has also a disinfecting action, may prevent bacterial changes in the wet coagulum, and also in this way influence the properties of the resulting dry rubber. We will discuss these points in the following paragraphs.

§ 42. Ammonia.

This is the oldest anti-coagulant, used many years ago in preserving latex for shipment to Europe. Usually rather

large quantities, such as 2 to 5% of the latex, are added in such cases. For this purpose, the preservation of latex over a long period, it is still the best medium, since it keeps the latex pretty well unchanged, at least so far as its fluidity and state of suspension go: no clotting or other beginning of coagulation occurs. Whether in the long run the proteins and other constituents of latex remain unaffected in an ammoniacal solution, remains to be investigated. For later investigation, the ammonia is easily removed by dialysis.

On latex preserved with ammonia see, for instance, V. HENRI *Le Latex*, page 323; CL. BEADLE and H. P. STEVENS, VIII Int. Congr. IX, 19, also Z. Koll. 13 (1913), 208; P. DEKKER, *Comm. Delft I*, 24.

Though ammonia was used on estates in the first years of plantation-rubber, when ammoniated water was put into the cups or pails, it is now completely out of use, because other substances are cheaper and better.

Some figures for the decrease in percentage of lump and scrap, when using dilute ammonia on the tapping cut, are given by W. LUCAS (*Bull. Ass. Pl.* 4 (1912), 123):

J. C. HARTJENS (*Arch.* 2 (1918), 168) in one experiment found the effect of ammonia added as an anti-coagulant in the field (8 cc of a 5% solution per liter of latex) to be nil.

The effect of ammonia or rather of ammonium salts, which are formed from the ammonia in coagulation by acids, is to retard vulcanisation somewhat.

B. J. EATON (*Agric. Bull. F. M. S.* 6 (1917), 148; *Bull. F. M. S.* No. 27 (1918), 312) mentions that ammonia greatly retards the rate of cure of the rubber (matured rubber?); slabs of fresh coagulum, soaked in ammonia for 24 hours did not show the ordinary increase in rate of cure due to maturation.

In experiments made by L. E. CAMPBELL (*Bull. Ceyl.* No. 23 (1915); *Bull. Imp. Inst.* 14 (1916), 511) the addition of a small amount (0.0056%) of ammonia to the latex retarded the rate of cure of the unsmoked sheet somewhat, whilst the tensile strength and chemical composition of the rubber remained unchanged.

It may further be mentioned that the viscosity of latex is much diminished by the addition of ammonia, as we have seen in § 16. This, of course, aids in straining and prevents clotting.

§ 43. Formalin.

Formalin also was already in use in former times to preserve latex. It is, however, not so suitable for this purpose as ammonia, because after some time a beginning of curdling or clotting sets in.

See CL. BEADLE and H. P. STEVENS (VIII Int. Congr. IX, 17; also Z. Koll. 13 (1913), 207), who recommend an addition of 2 to 3 % of formalin, suitably diluted, for preserving the latex.

For practical use on estates formalin is one of the commonly used anti-coagulants. It has a strong anti-coagulating effect, but is less favourable in its effect on the quality of the rubber. Small quantities, such as the common dose of $\frac{1}{2}$ cc. of commercial formalin (containing appr. 40 % of formaldehyde) per liter of latex, cause insignificant changes, which a good estate-rubber can easily bear; but in greater quantities, — (and what estate can guarantee that these will never occur in actual practice, by mistake, or through lack of supervision) — the injurious effect is greater than may be permitted. The figures below give a brief summary of the effect of formalin on the properties of the rubber.

	Formalin per liter of latex	
	$\frac{1}{4}$ —1 cc.	2—4 cc.
Decrease in tensile strength	0.0 to 0.02	0.0 to 0.08
Increase in time of cure. .	2 to 5 minutes	5 to 15 minutes
Increase in slope	0 to $\frac{1}{2}$	$\frac{1}{2}$ to $1\frac{1}{2}$
Decrease in viscosity . . .	1 to 3	$1\frac{1}{2}$ to 6

See O. DE VRIES, Arch. 2 (1918), 80 and 98.

The above figures apply to crepe; for smoked sheet, which is not so thoroughly washed in rolling, the effect may be greater, depending upon the method of preparation, and principally upon the proportion of formalin that is kept absorbed in the sheet.

As will be seen from the above table, the use of formalin tends to cause a deterioration of all properties, and when 2—4 cc. of formalin are used the deterioration may become serious.

As mentioned above, the effect of chemicals such as formalin is complex. In the first place they may act directly as a chemical or catalyser, so to say by themselves, and in the second place as a disinfectant, retarding bacterial changes in the wet coagulum. The following figures for time of cure form a good example:

	Rolled 2 hours after coagulation	Rolled 24 hours after coagulation
Without formalin . . .	130 minutes	120 minutes
With " . . .	135 "	135 "

O. DE VRIES, Arch. 2 (1918), 84.

In the crepes which were rolled directly after coagulation, the formalin had therefore caused a decrease in rate of cure of 5 minutes ($4\frac{0}{10}$), but in the crepes which were rolled the following day, the difference amounted to 15 minutes ($12\frac{1}{2}\frac{0}{10}$). From a comparison of the figures it will be clear that it is not the formalin which further retarded the rate of cure — since both samples with formalin need 135 minutes — but that the formalin hindered the acceleration or maturation, which brought the control-sample up from 130 to 120 minutes.

That formalin in itself, as a chemical, has a retarding effect, may be proved (see O. DE VRIES, Arch. 2 (1918), 82 and 98) by soaking fresh, wet crepe, or crepe already air dried in dilute formalin. The effect may be:

	Time of cure
Freshly rolled crepe directly hung to dry (control)	130 minutes
Freshly rolled crepe, soaked in formalin, then hung to dry	150 "
Freshly rolled crepe, soaked in formalin, then rewashed and recreped, and hung to dry	145 "
Dry crepe soaked in formalin and again hung to dry	140 "

The decrease in rate of cure is marked.

To avoid the extracting influence of the dilute formalin solutions, and thus make the experiments more conclusive, wet or dry crepes were also placed in vapours of formalin, i. e. above a formalin-solution; with the effect that the time of cure was increased by 4 and 17 % respectively (l. c. page 83). Further, powdered solid para-formaldehyde was added to the crepe prior to vulcanisation, at the time when the sulphur was mixed in; the increase in time of cure caused by addition of 0.2 % was 6 %, and when 1 % in weight was added, even 75 % (l. c. page 84 and 99).

In the same way B. J. EATON and J. GRANTHAM (J. S. Ch. I. 35 (1916), 718; also I. R. J. 52 (1916), 271; Bull. F. M. S. 27 (1918), 62 and 66) found a decrease in rate of cure of 30 to 50 % by soaking freshly rolled crepe or sheet in formalin. A retardation of 30 % was obtained by immersing dry rapid curing crepe (from matured rubber) in formalin.

The effect of formalin on the process of maturation is very marked. Slabs made from latex containing formalin, or slabs soaked in formalin shortly after coagulation and then left to mature, do not show an increased rate of cure, so that maturation may be wholly prohibited. Soaking the slab in formalin after maturation has taken place to some extent, or after maturation is finished, also gives a large diminution in rate of cure. (EATON and GRANTHAM, l. c.)

In experiments by L. E. CAMPBELL (Bull. Ceyl. 23 (1915); Bull. Imp. Inst. 14 (1916), 512) the addition of a large amount of formalin (0.5 %) to the latex (the coagulum being rolled next day) lengthened the time of vulcanisation of unsmoked sheet considerably (40—100 %). Keeping the formalined latex for 3 or 6 days before coagulation, reduced the increase in time of cure somewhat. Neither the tensile strength nor the

chemical composition showed marked deviations, when formalin was used. See also Bull. Ceyl. No. 35 (1917); Bull. Imp. Inst. 16 (1918), 434.

A. J. ULTÉE (Arch. 2 (1918), 344) found that, comparing rubbers from latex to which formalin, sodium sulphite and washing soda respectively were added as anti-coagulants, formalin gives rubber with the lowest, and sulphite that with the highest viscosity.

On the colour of the rubber formalin has a certain effect; especially in sheet-rubber it keeps the colour paler and more yellow.

The influence of formalin on the velocity of drying of the coagulum will be treated in § 106.

§ 44. Sodium sulphite.

In contrast with formalin, sodium sulphite has a favourable effect on the properties of the rubber, and it might be most warmly recommended as an anti-coagulant if it did not have another drawback, namely that it retards the drying of the rubber. In crepe and thinly rolled sheet this may have no practical significance, but in thicker sheet it may become very troublesome and make one prefer the use of another anti-coagulant.

Sodium sulphite is used preferably in the crystalline, hydrated form $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, which, when pure, contains 25.4% of SO_2 ; the less stable, pulverised, anhydrous form Na_2SO_3 should contain 50.8% SO_2 . The latter salt quickly absorbs water from the air; both salts are unstable and liable to oxydation. Unless they are kept in tightly closed receptacles, they rapidly change and lose their anti-coagulating effect.

The effect upon the rubber of the usual quantities of 1.2 gr. of crystallized sodium sulphite, made up f.i. in a 10% solution, per liter of latex, is as follows:

Increase in tensile strength.	0.0 to 0.03
Decrease in time of cure	5 to 10 minutes
Decrease in slope.	1 to 1½
Increase in viscosity.	1 to 2

which figures may be greater for sheetrubber, depending upon circumstances. Though the difference is not of much importance, it will be seen that all properties are improved by the use of this anti-coagulant.

See O. DE VRIES, Arch. 2 (1918), 77 and 97.

Experiments made by L. E. CAMPBELL in Ceylon (Bull. Ceyl. No. 23 (1915); Bull. Imp. Inst. 14 (1916), 512) gave once a decrease, another time no difference in rate of cure, when a 2 % of sodium sulphite was added to the latex and the coagulum rolled to sheet on the next day. The tensile strength and chemical composition of the rubber were not changed.

S. MORGAN (Prep. Pl. Rubber, 50) mentions that, in the usual quantities, sodium sulphite is of no influence on the properties of the rubber.

On the colour of the rubber the sodium sulphite has naturally a bleaching effect similar to that of bisulphite, but less strong, in conformity with its lower SO_2 -content.

Under certain circumstances, which are not yet wholly cleared up, sodium sulphite may further the formation of darker and lighter coloured patches on sheetrubber during drying; in such cases soda is to be preferred as an anti-coagulant.

See J. C. HARTJENS, Arch. 4 (1920), 159.

Whilst there is little doubt that the anti-coagulating action of formalin may be ascribed to its disinfecting action, and that of soda and ammonia to their alkaline character, the cause of the anti-coagulating effect of sodium sulphite is not yet wholly cleared up. This salt has an alkaline reaction, and as such may act in the same way as ammonia, in neutralizing the acids spontaneously formed in the latex. At the same time the disinfecting action of the salt itself, or of the SO_2 formed from it, may play a role. In this connection it is interesting to note that of the more strongly alkaline soda (see § 45) a larger proportion is necessary to reach the same anti-coagulating effect as with sodium sulphite; whilst sodium bisulphite, which contains more SO_2 but has an acid reaction, has a smaller anti-coagulating effect, and in some circumstances may aid coagulation or clotting. Probably,

in sodium sulphite, both alkalinity and disinfecting action play a role; but this point is not yet sufficiently cleared up.

When using sodium sulphite as anti-coagulant, it should not be forgotten that somewhat more acetic acid must be added in coagulation to neutralise the sodium sulphite.

§ 45. Soda and other anti-coagulants.

Soda acts as an anti-coagulant because of its alkalinity. It has little or no effect as a disinfectant, and perhaps on this account its action is in some cases not very strong. But on the other hand soda does not retard the drying of the rubber, which causes it to be sometimes preferred to sodium sulphite.

A drawback however to its use in the preparation of sheetrubber is, that it may give rise to bubbles of the carbon dioxyde formed from it.

In certain districts with a calcarious soil the anti-coagulating effect of soda is somewhat better than that of sodium sulphite.

J. C. HARTJENS, Arch. 2 (1918), 166 and 184.

As an anti-coagulant the ordinary crystallised washing soda $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ may be used which, however, on keeping loses part of its water-content. The stable, powdered, anhydrous form is therefore preferred, but often contains small amount (10 — 20 %) of moisture, and should therefore — as, by the way, should all chemicals used — be analysed before use.

The effect of soda on the inner qualities of rubber is very small and not unfavourable. The usual amount of 1 gm. of anhydrous soda per liter of latex gives about the following results:

Increase in tensile strength.	0.0 to 0.04
Decrease in time of cure	3 to 10 minutes
Decrease in slope.	0 to 1
Increase in viscosity.	1 to 2

See O. DE VRIES, Arch. 2 (1918), 85 and 100.

Soaking the finished crepe in a soda-solution is, of course, not comparable to adding soda to the latex, as in the former case the rubber is impregnated with the alkaline-solution, whilst in the latter the soda is acidified by the acid used in coagulation.

Soaking slab (matured coagulum) in soda gives a marked increase in rate of cure, the ordinary effect of adding alkalies to the rubber; see B. J. EATON, Agric. Bull. F. M. S. 4 (1915), 30.

There are a great number of other substances of which the anti-coagulating qualities have been investigated, amongst which we may cite *borax*, *boracic acid*, *sodium hydroxyde*, *sodium oxalate* and *sodium fluoride*. None of these has established itself in use and little is yet known of their influence on the properties of rubber. Hence a discussion or summation of their effects may be omitted here.

See, for instance, B. J. EATON, Agric. Bull. F. M. S. 6 (1917), 148 and Bull. F. M. S. No. 27 (1918), 295 and 307; J. C. HARTJENS, Arch 2 (1918), 168 and 184.

§ 46. Disinfectants.

In ordinary estate-practice it is rarely necessary to add special disinfectants to the latex. The disinfecting action of the anti-coagulants just named (especially formalin) may serve if it is necessary. In case one has an epidemic of spots caused by bacteria or moulds (see § 167), a disinfectant may be mixed with the latex as a precaution, so long as one is not certain that the infection is eradicated.

The best and most commonly used disinfectant is chinisol, a yellow crystalline substance, of which one commonly uses 0.1 gm (in 1 % solution for example) per liter of latex. So far as investigated chinisol leaves the properties of the rubber unchanged. It is an excellent aid in such circumstances as those mentioned above, but is rather too expensive for general use.

In methods of preparation in which the coagulum is not rolled and dried, but is worked into thick moisture-holding slabs or blocks, a disinfectant is also sometimes added to the latex to protect the rubber from decay (infection, moulds, etc.). In such cases one finds the use of creosote mentioned.

The use of creosote in alcoholic solution, added in an amount equal to 0.5 % to the latex, was recommended by J. PARKIN (Circ. R. B. G. 1 (1899), 150) to prevent the growth of moulds during the drying of (unsmoked) sheets or biscuits. Phenol was found to evaporate too quickly for this purpose; heating the latex was recommended in this process, as creosote does not well mix with the latex in the cold.

J. C. WILLIS and M. K. BAMBER (Circ. R. B. G. 4 (1907), 1; Trop. Agric. 1907 Suppl., 98) studied the preparation of creosoted blockrubber, containing 7 % of moisture, as an analogy to the Brazilian method of preparation (compare § 191).

In experiments made by L. E. CAMPBELL (Bull. Ceyl. No. 27 (1916), 21; Bull. Imp. Inst. 14 (1916), 536) the addition of an alkaline creosote-solution to the latex was proved to be without influence on the tensile strength and rate of cure of the rubber. In further experiments however (Bull. Ceyl. No. 35 (1917) 6; Bull. Imp. Inst. 16 (1918), 434) the rate of cure was found to be decreased by the addition of alkaline creosote to the latex. The chemical composition of the rubber showed no marked effect by the use of creosote in the latex.

β -Naphthol, boracic acid and such substances are also in use; but their effect on the rubber is not yet sufficiently known.

On the use of β -naphthol and other phenols in latex or for immersion of the coagulum, see patent-description I. R. J. 56 (1918), 122; J. S. Ch. I. 37 (1918), 313 A.

Boracic acid, when added to the dry rubber before vulcanisation, has a retarding effect, acting as a negative catalyst like most acids (B. J. EATON, Agric. Bull. F. M. S. 6 (1918), 147 and 423). This, of course, is distinct from its action as a disinfectant when added to the latex prior to coagulation, in which case its influence on the rubber has not yet been investigated.

The use of phenol was recommended some time ago, in combination with sulphuric acid, as a coagulant (see § 86). Phenol and similar substances give the rubber a very dark colour, and consequently can not be used for the ordinary estate-products. The rate of cure is decreased by their use.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 497; also I. R. J. 51 (1916), 792) found that phenolic substances retard the rate of cure, and cause a decrease in tensile strength and type (slope).

B. J. EATON and G. S. WHITBY (Agric. Bull. F. M. S. 5 (1917), 124; see also Bull. F. M. S. 27 (1918), 250) found that phenol and cresol, added to the latex, retard the rate of cure of smoked sheet by appr. 10%, and cause rapid oxydation and darkening.

On the use of chinisol and phenol see also J. C. HARTJENS, Arch. 2 (1918), 169 and 184.

§ 47. Anti-oxydants.

When preparing pale crepe, every discolouration must be avoided, as it affects the value of the crepe on the market. An anti-oxydant is therefore generally added to prevent surface-oxydation or discolouration caused by oxydases (see § 12) or other agents. In preparing smoked sheet, the brown colour of the smoke generally neutralises any difference in tint caused by the above named factors, and the use of an anti-oxydant is necessary only during periods when the tendency to discolouration of latex is very high, for instance, shortly after wintering (see § 21).

For a general discussion of the arguments for, and methods of, preparing a rubber of uniform pale colour, see CL. BEADLE and H. P. STEVENS, Rubb. Rec. 1914, 357.

The substances used for this purpose are often called bleaching agents, but this term is not precise. If one adds bisulphite or some similar substance to the latex, then, even after the addition of acetic acid, the latex looks quite the same as when no anti-oxydant is added. It is only gradually that the coagulum without anti-oxydant takes on a darker colour; either brownish, or (in case of strong oxydase-action) violet. Meanwhile the coagulum with the anti-oxydant keeps its original white colour unchanged. These substances therefore do not take away an existing colouring, but prevent the development of discolouration.

§ 48. Sodium bisulphite.

The principal anti-oxydant is sodium bisulphite, which is used in the form of a dry white powder, containing, when pure, 61.5% SO_2 . On exposure to the air, however,

it soon loses in strength. Special care is necessary to protect it from contact with the air by keeping it in tightly closed vessels, and control by occasional analyses may prevent many deceptions.

Added in the usual quantity of $\frac{1}{2}$ to 1 gram per liter of latex in the preparation of crepe-rubber, bisulphite gives only a small change in the properties of the rubber, and this in the desired direction. The following may give an idea of the changes produced.

	$\frac{1}{2}$ — 1 gm.	2 gms.
Increase in tensile strength. .	0.0 to 0.05	0.0 to 0.05
Decrease in time of cure. . .	5 to 10 min.	10 to 15 min.
Decrease in slope.	1 to $1\frac{1}{2}$	1 to $1\frac{1}{2}$
Increase in viscosity. . . .	$1\frac{1}{2}$ to 10	3 to 13

In all qualities therefore a slight improvement is found.

See O. DE VRIES, Arch. 2 (1918), 87 and 101.

These changes may be explained as follows. The increase in rate of cure is caused by the bisulphite being a sodium salt, and thus strengthening the alkaline element of the latex; sodium acetate, which is formed from the bisulphite and the acetic acid, has the same effect (see § 52). The decrease in slope is caused by the sulphurous acid, which the acetic acid sets free from the bisulphite and which prevents oxydation. Bisulphite has in this respect the same effect as the anti-coagulant sodium sulphite, which fact is easily understood, since both are sulphurous salts of sodium. In sodium sulphite, sodium, the alkaline element, predominates and this, in addition to its disinfecting power, probably gives the effect as an anti-coagulant. On the other hand bisulphite, as the name indicates, contains a double quantity of sulphurous acid; its reaction is acid and as an anti-coagulant it has only a slight effect, due to its disinfecting power. It acts, however, much more strongly against oxydation than the sulphite.

The effect of bisulphite mentioned above may be found when the coagulum is rolled shortly after coagulation. It may be considered as the direct effect of adding the bisulphite, which then has a chemical, and to some extent a catalytic action during vulcanisation.

If the time between coagulation and rolling is longer, then under ordinary circumstances changes in the coagulum occur, which accelerate the vulcanisation somewhat and increase the viscosity. This will be further discussed in § 107 and 108.

Bisulphite, as a disinfectant, retards these changes. The speed with which the changes take place in a given latex, and the length of time between coagulation and milling, determine what the effect shall be.

The following table gives a good example of the effect of bisulphite. Coagulum was prepared from the same latex with and without bisulphite. Half of each mass of coagulum was worked 2 hours after coagulation, the other half 24 hours after coagulation, the times of cure being as follows.

	Rolled after 2 hours	Rolled after 24 hours
Without bisulphite	130 minutes	115 minutes
With „	125 „	120 „

See O. DE VRIES, Arch. 2 (1918), 89 and 102.

Comparing the crepes which were rolled shortly after coagulation, the bisulphite is seen to have an accelerating effect; but if the crepes, rolled after 24 hours, are compared, the one with bisulphite is found to vulcanise more slowly. It may further be clearly seen that this effect is not a „retarding” of the vulcanisation, but a „prevention of acceleration”. The bisulphite-crepe during the night becomes accelerated in rate of cure by 5 minutes; the crepe without bisulphite, however, matures to a much greater degree, the time of cure decreasing by 15 minutes, and with this decrease surpassing the bisulphite-crepe in rate of cure.

The phenomena therefore are the same as those already des-

cribed for formalin, with only the difference that the formalin has, both as a catalyser and as a disinfectant, a retarding action, while bisulphite as a catalyser accelerates the cure, but as a disinfectant retards it.

One may therefore expect a variable effect by the use of bisulphite depending upon the methods followed. But it will be clear that the use of bisulphite tends to reduce very largely the differences caused by variations in length of time which elapses between coagulation and rolling. As we shall see in § 117 and 131, irregularity in treatment of the coagulum is one of the causes (they are rather few) of variability in the preparation of crepe-rubber. Bisulphite decreases this variability to a great extent, because it prevents decomposition (maturation) in the coagulum.

In general, therefore, the use of bisulphite, in addition to its good effect on the appearance of the rubber, also tends to improve the properties of the rubber and to make the product more uniform. The use of bisulphite can therefore be recommended, so far as it is profitable.

In the preparation of sheet-rubber bisulphite finds an application only in the times when there is difficulty with violet colouring in the coagulum (oxydases in the latex). One can then add a little bisulphite to the latex, or better still can pour a little dilute bisulphite solution (of about $\frac{1}{2}$ 0/0 strength) over the coagulum as soon as it is sufficiently hardened.

Excluding the air from the coagulum is the end desired here, and this can also be done by pouring water over the coagulum or by keeping the coagulum under water.

The result of immersing in bisulphite-solution after coagulation is not the same as when the bisulphite is added to the latex before coagulation. It may cause a slight retardation in rate of cure. When one adds bisulphite before coagulation, it is changed by the acetic acid into sodium acetate and sulphurous acid, while if one treats the coagulum externally with bisulphite after coagulation, little or none of the bisulphite is changed, according to the way in which it comes into contact with the acetic

acid, and the effect on the properties of the rubber will depend upon the manner in which the coagulum is further treated.

The first published prescription for the use of bisulphite is due to M. BARROWCLIFF (*Agric. Bull. F. M. S.* 1 (1912), 10).

The inventors, CL. BEADLE, H. P. STEVENS and S. MORGAN, later (*I. R. J.* 46 (1913), 222; *Prep. Pl. Rubber* page 69; see also *Rubb. Rec.* 1914, 357) gave a detailed description of their experiments, especially to prove that the use of bisulphite is not injurious to the rubber. The differences in tensile strength or deformation after five extensions, though small, were in favour of the bisulphite-samples, even after 12 month's ageing. These investigators further found that the time of drying of the rubber is somewhat prolonged by the use of bisulphite and that (even when using unnecessarily large quantities of bisulphite) no traces of it can be detected in the ash of the crepe in the form of sulphate.

On the other hand the use of chemicals, especially bisulphite, was opposed by W. A. WILLIAMS (*Rubb. Ind.* 1914, 291) who however based his conclusions on experiments in which bisulphite was added to the dry rubber just before vulcanisation, in which case it retards vulcanisation greatly, and diminishes the tensile strength. This, of course, is not comparable to adding the chemical to the latex before the addition of acetic acid. See discussion *ibid.* page 295, and *Proc. III^d Congr.* 1914, 145. For further discussion see *I. R. J.* 46 (1913), 352 and 540.

B. J. EATON and J. GRANTHAM (*Agric. Bull. F. M. S.* 3 (1915), 225 and 445; *Bull. F. M. S.* No. 27 (1918), 210) found no important effect of the use of bisulphite on tensile strength and rate of cure when the coagulum was made into crepe on the day following coagulation. In most cases a small decrease in rate of cure was found; in others a small increase. The addition of bisulphite to the latex has a distinctly retarding effect on the processes of maturation (compare § 108) because of its disinfecting action.

A. J. ULTÉE (*Rubb. Rec.* 1914, 392; *Arch.* 2 (1918), 334 and 345) found that bisulphite increases the viscosity of the rubber somewhat; for crepe-rubber the increase is from 0 to 30% and for sheet from 16 to 43%. He further stated that it causes no increase in ash-content of the rubber, so that the supposition that sodium acetate is the cause of the slower drying of the rubber is probably not correct.

Experiments made by L. E. CAMPBELL (*Bull. Imp. Inst.* 16 (1918), 440), in which from 0.1 to 2 gm of bisulphite were added per liter of latex, and the coagulum was rolled to crepe

the next day, showed no change in tensile strength caused by the addition of bisulphite. The rate of cure, however, was slightly lowered by the small dose, and somewhat increased by the larger (2 gm) dose, which result is not contrary to the one given above.

The Government Institute at Delft (Holland) also found rubber prepared with not too large quantities of bisulphite to be equal in quality to rubber prepared without bisulphite (Comm. Delft I, 34).

A review of the arguments for and against bisulphite and of the discussions following its introduction, is given by V. CAYLA (C. Gp. 1915, page 8705).

Since bisulphite retards coagulation to some extent — or neutralises some acetic acid — a larger proportion of acid must be added when bisulphite is used, to obtain a coagulum of the same stiffness in the same time. For the usual quantity of $\frac{1}{2}$ gm to 1 gm bisulphite per liter of latex to be coagulated, the acetic acid has to be increased by $\frac{1}{4}$. In making crepe rubber, and especially when the coagulum is left undisturbed until the following morning and has time enough to harden, this point is not of so much importance. But when sheet rubber is made, and some bisulphite is used in the latex in the time of increased tendency to violet discolouration (see § 12), care must be taken to increase the acetic acid proportionately. Especially when the sheet is rolled the afternoon after coagulation, the coagulum may be still too weak, and the fresh sheet likely to stretch.

Sometimes the method is followed of adding bisulphite-solution to the latex and then waiting half an hour before adding the acetic acid, „to give the bisulphite time to work”. This is quite unnecessary; acetic acid may be added directly after, or even at the same time as the bisulphite, provided the solutions are well stirred in the latex and into the corners and along the walls of the tank before the latex gets too thick. Bisulphite in an acetic acid solution works as well as in ordinary latex, which itself has considerable acidity (See § 9).

The addition of sodium bisulphite to the latex somewhat retards the rate of drying of the rubber. For the usual dose of 1 gm per liter of latex the crepe may take 1 to 2 days

longer to dry; larger doses, such as 2 gm may retard the drying considerably, and an addition of $\frac{1}{4}$ to $\frac{1}{2}$ gm in sheet-preparation also makes itself felt in a prolonged time for drying and smoking.

§ 49. Sodium thiosulphate (hyposulphite).

In the time when sodium bisulphite was scarce and expensive, sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, the common „hypo” of the photographers was used as an anti-oxydant on some estates.

This substance, however, does not compare with bisulphite as an anti-oxydant; its effect is much weaker, so that more of it must be used, and the expense is therefore much greater.

The use of thiosulphate has little effect on the properties of the rubber. The rate of cure and the viscosity decrease slightly, but the variations have no practical significance.

See O. DE VRIES, Arch. 2 (1918), 91 and 102.

A. J. ULTÉE (Arch. 2 (1918), 336 and 345) found a small decrease in viscosity caused by the use of thiosulphate.

It may be mentioned that for some time a special effect was expected from the use of hyposulphite. This chemical, when acid is added, gives a precipitate of sulphur, so that some sulphur, very finely divided, will be left distributed in the rubber when it has been coagulated by acetic acid. Since sulphur is used in vulcanisation, it was hoped that a favourable result would be secured by the finely divided sulphur, and plans were even made to distribute sulphur and other substances, such as colouring matters etc., evenly through the latex, so that manufacturers would no longer need to add these to the rubber. But nothing came of this in practice; manufacturers prefer to make their own mixtures according to their own formula, and, so far as thiosulphate is concerned, no effect of the precipitated sulphur could be stated.

See M. K. BAMBER, Ceyl. R. E. 1916, 46 and 50; Trop. Agric. 27 (1906), 28 and 280. See further L. MORISSE, Le Latex, page 423.

§ 50. Blankite, rongalite.

From some quarters still other sulphur-compounds have been proposed as anti-oxydants; thus blankite, sodium hydro-sulphite $\text{Na}_2\text{S}_2\text{O}_4$, has been used now and then on an experimental scale.

This substance may decrease the viscosity of the rubber somewhat; no data are available as to its influence on the properties after vulcanisation.

A. J. ULTÉE (Rubb. Rec. 1914, 394; Arch. 2 (1918), 335 and 345).

For a patent-description on this substance see G. EICHELBAUM, Z. Koll. 12 (1913), 210.

Other substances, for example rongalite (a compound of formaldehyde-sodium-hydrosulphite and sodium-sulphite), have been suggested as very strong anti-oxydants. These substances are more expensive than bisulphite and have therefore found no application. Nothing is known of their influence on the properties of rubber.

See A. DUBOSC, C. Gp. 1916, 9031.

§ 51. Other anti-oxydants.

It may be mentioned that there are other substances which can prevent oxydation. For example, this is known to be true for acetic acid when used in large quantities (see also § 83); formerly these were very generally used for this purpose, before bisulphite had made its entry.

A strong dose of alum (for instance 10 gm or more per liter of latex) also gives a pale rubber; but this medium is not at all to be recommended, since it causes deterioration of the qualities after vulcanisation and decreases the viscosity (see § 88).

The same is to be said for large quantities of sulphuric acid (see § 86) and hydrochloric acid. Hydrofluoric acid, which was recommended in the form of „Purub“, also produces pale rubber (see § 89), and the same is the case with oxalic acid and several other substances, none of which, however, can compare with the combination of sodium bisulphite and acetic acid.

Finally we may add that heating the latex or the coagulum above 70° C renders the oxydase inactive and thus prevents oxydation.

The destroying of the enzymes by heat was advocated by M. K. BAMBER Agric. Bull. Str. F.M.S. 7 (1908), 347; also Trop. Agric. 31 (1908), 300, who indicated the following three ways in which this could be accomplished:

- 1) by passing steam into the bulked latex and maintaining its temperature for 15 minutes at 80° C;
- 2) by immersing the rolled biscuits or sheets in hot water;
- 3) by employing hot water or steam-heated rolls in the washing machine.

Heating the latex (defecation) has been in use in former years on many estates, but was completely dropped when bisulphite came in vogue.

See M. K. BAMBER, Lectures 1908 page 73; A. J. ULTÉE Rubb. Rec. 1914, page 392.

Heating the coagulum was often used formerly. It is, however, not without its serious drawbacks, as it injures the properties of the rubber (see § 100 and 140).

§ 52. Sodium acetate, sodium sulphate and sulphurous acid.

A few words may here be added about the effect of certain chemicals, which are generally not added as such to the latex, but which are formed from the most common anti-coagulants and anti-oxydants, sodium sulphite and sodium bisulphite. We refer to sodium acetate, which is formed from both the above (and all other) sodium salts on the addition of acetic acid; to sulphurous acid, and to sodium sulphate, which is formed from both salts by oxydation and generally is contained in the commercial products to some extent.

Sodium acetate, when added as such to the latex, accelerates the rate of cure and increases the viscosity by the same amount as the corresponding quantities of sodium sulphite and bisulphite. The tensile strength is a little increased in connexion with the higher rate of cure; and the

figure for slope is found to be somewhat smaller. It retards coagulation markedly, as was to be expected: it diminishes the acidity of acetic acid because the degree of ionisation is lessened by the addition of an acetate. Sodium acetate does not, as was formerly supposed, retard the rate of drying of the rubber by its hygroscopic properties; on the contrary, large quantities seem to accelerate drying somewhat.

See O. DE VRIES, Arch. 2 (1918), 92 and 103. B. J. EATON (Bull. F. M. S. 17 (1912), 22) found the coagulating effect of hydrochloric acid also to be diminished by the addition of sodium acetate.

M. BARROWCLIFF (Agric. Bull. F. M. S. 1 (1912), 11) supposed the slower drying caused by bisulphite to be due to the sodium acetate formed from it. A. J. ULTÉE (Rubb. Rec. (1914), 392) argued that this is improbable, as no traces of the excess sodium salts can be detected in the ash of the rubber.

It may be added that soaking dry crepe in a sodium acetate solution gives a marked acceleration of vulcanisation. In this way the effect of such a chemical is proved more conclusively than by adding it to the latex before coagulation. The effect may be compared with that of soaking the crepe in sodium hydroxyde solution (see § 106).

O. DE VRIES, Arch. 2 (1918), 93 and 103.

Sulphurous acid, when added to the latex or used as a coagulant (see § 89), gives a pale-coloured rubber and, as might be expected, prevents surface-oxydation and darkening. In quantities corresponding to the ordinary doses of sulphite and bisulphite it is without effect on the rate of cure, whilst the tensile strength and viscosity increase somewhat, and the slope diminishes (improves) markedly. The rate of drying, however, seems to be somewhat lowered by the use of sulphurous acid.

O. DE VRIES, Arch. 2 (1918), 94 and 103.

Sodium sulphate, when added to the latex even in much larger quantities than are ever present in sulphite or bisulphite (for instance, 1 or even 4 gms per liter of latex) is, so far as investigated, without influence on the properties of the rubber.

It will be clear from the above, that the acceleration in rate of cure caused by both sodium sulphite and bisulphite (when acting only chemically) is caused by the sodium-ion. The increase in viscosity is explained by the effect of both the sodium and the sulphurous ion; whilst the decrease in slope is due principally to the action of the sulphurous acid, which, of course, is also responsible for the pale colour. Finally the lower rate of drying seems to be caused by the sulphurous acid, and certainly is not caused by the sodium acetate.

CHAPTER IV.

MIXING THE LATEX AND BRINGING TO STANDARD DILUTION.

§ 53. Mixing the latex.

After what was said in Chapter II and especially in § 37, no further proof is needed that the mixing of the greatest possible quantities of latex is in the highest degree desirable for securing a uniform product. The numerous factors which cause variation in the composition of the latex, and thereby variation in properties of the rubber, bring it about that from almost every separate group of trees a rubber is secured with a somewhat different combination of properties. This goes so far that one can sometimes decide, from an examination of the inner qualities of samples of the rubber from a given estate, from which division it has come. An example for the time of cure may serve to make this clear.

Division	June 1916		July 1916			October 1916	March 1917
	6	7	20	21	22		
I	115	110	115	115	115	—	—
II	125	125	125	125	125	105	110
III	110	110	—	—	115	—	—
IV	105	105	—	—	110	—	—

It will be seen that Division II gave the rubber which vulcanised most slowly in June and in July, whilst the product from Division IV vulcanised most rapidly. Naturally such values are not constant over long periods, for the condition of the plots changes. Division II gave, in October 1916 and March 1917, a product which vulcanised more rapidly, perhaps because younger trees were brought into tapping.

Mixing the latex renders these variations for the most part insignificant. The rubber becomes uniform in its inner qualities, and in most cases comes nearer the general average figures, which fact is desirable for a mass-product like rubber.

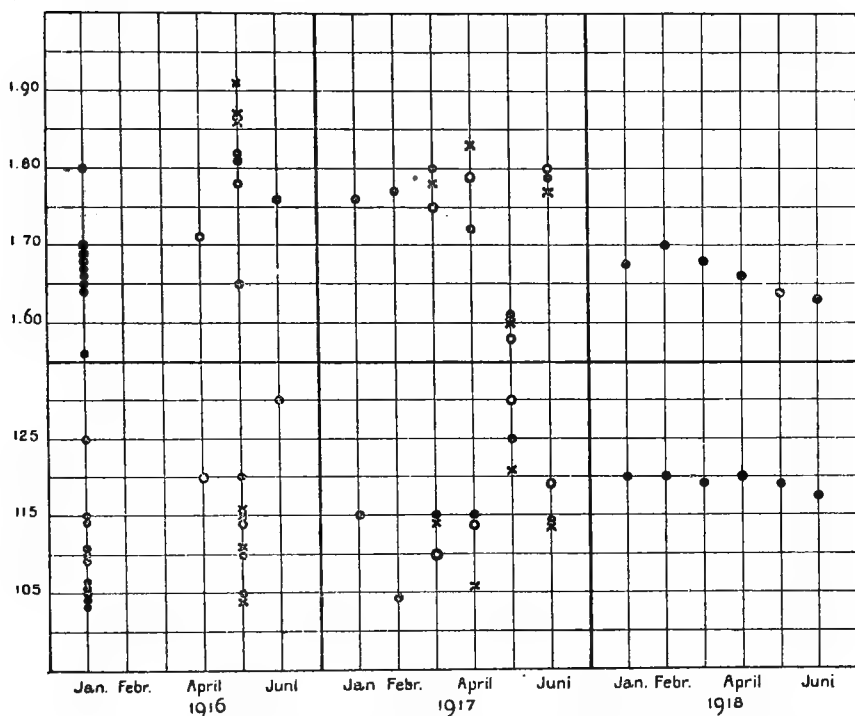


Fig. 3.

Viscosity and standard time of cure for samples of one estate in subsequent years. Improvement in uniformity by adopting standard methods of preparation. (Viscosity expressed as Viscosity Index, see Chapter XX).

We will now give an example of the influence which mixing the latex can have on viscosity and rate of cure. Figure 3 gives these figures for the first half year of 1916, 1917, and 1918 for an estate which makes crepe. In 1916 the latex was received and coagulated in jars, partly by divisions and partly by tapping fields; it was not diluted to 15 % and was not mixed. In January we tested the product of one division for ten successive days. In May we

tested the product from various tapping fields (jars), further we tested some more samples in April and June. The values differ markedly, from 105 to 130 minutes for time of cure and from 1.56 to 1.91 for viscosity; therefore for both properties the variations range beyond the normal limits for crepe.

In 1917 the latex was diluted to 15 %, but still kept separate in jars. Apparently the method of preparation was not very well arranged, the values still lie too far from each other, and the three divisions (as indicated by various signs in Fig. 3) regularly gave noticeable differences.

In 1918 a mixing tank was used and the latex was diluted to a standard rubber-content of 15 %. The effect is striking, the values for time of cure are very constant. The practical advantage of standardised methods of working was also very apparent; the work in the factory was simpler, as the operations were more similar from day to day, and the properties of the coagulum more constant. The drying of the crepe was more regular, as the thickness and hardness of the fresh crepe were nearly the same from day to day; and the grading was much simpler, as the difference in colour disappeared and the product became much more uniform in outer appearance. The consequence was that more time was available for careful preparation.

There are however, as indeed with all good things, some drawbacks to the use of the mixing tank. The mixing of all the latex would mean, for some estates, transportation of latex over long distances, sometimes over difficult paths, through ravines, etc. Also apart from the actual difficulties of transporting large volumes of latex under such circumstances, the cost of transporting dry rubber or wet coagulum will always be less than that of transporting the latex. Again, the transport of latex from far distant divisions, especially when it has to be done by coolies or on horse-back, takes a long time. The latex, when tapping is begun at six, and collecting is done at nine or ten o'clock in the morning, should be ready for coagulation at eleven or at the latest at twelve o'clock, and every hour later means a greater proportion of lump, curdling and premature coagulation, and therefore loss in first-latex rubber. The shaking

and jolting during transport, especially when pails are used, or when the cans are not filled to the cover, may further the formation of lump. Of course, the use of anti-coagulants (see Chapter III) may be of great help in preserving the latex during transport, as well as in the mixing tank in the factory, when waiting for the last tappers to arrive. But this means an increase in cost, and is not always effective, especially on rainy days, when the latex has a great tendency to clot.

Though these difficulties may in many cases be overcome by a proper arrangement of the work, it will be clear that local circumstances may differ greatly and sometimes make it cheaper and easier to coagulate the latex in several different places. In former years the bulking of latex, not only from one estate, but from several neighbouring estates, was often strongly recommended, and also put into practice, where transport could be simplified by narrow-gauge railways, motor-cars, etc. Theoretically, of course, the arguments set forth in Chapter II and in this paragraph all point to the desirability of mixing as large quantities of latex as possible; but practicability often dictates otherwise.

In our opinion the question should be decided from this point of view: mix as great quantities of latex as possible, at least that from several hundred acres; but do not carry this principle so far that a loss results either in an increased cost-price, or in a less sightly product, due to premature coagulation. Build, if necessary, two mixing tanks on divisions far distant from each other, or fill the mixing-tank in the factory twice, with the early and the late latex. The two sorts of rubber obtained by the last method will show small differences in properties, so that the estate will not secure in this way the highest degree of uniformity. However, if both quantities of latex are large, the differences will not be greater than those between different estates (perhaps 5 to 10 minutes in time of cure). One can then, if desirable, market these different kinds under different marks. Further the differences, that obtain in each special case, might be determined by testing the rubber.

The rule for mixing the latex should be: always mix very large quantities, the more the better, preferably all the

latex from an estate; but do not allow this principle to predominate over other more weighty considerations such as transportation, premature coagulation, etc. In such cases separate the latex into two parts, each fairly large.

The argument is sometimes given as an objection to the mixing tank, especially if it is not used as the coagulating tank also (that is if the latex is drawn from it to be coagulated in dishes or smaller tanks) that the latex on standing creams or at least gradually separates into an upper layer of higher rubber-content, and a lower layer containing less rubber. This opinion is founded on faulty observations, for instance, on insufficient mixing when the heavier water is poured into the tank with latex. Latex, as long as it is liquid, does not cream, the rubber-globules, though lighter than the serum, do not rise (compare § 18). Even a high column of latex, after several hours quiet standing, shows exactly the same rubber-content below and above. It is only when coagulation or curdling sets in, that the clots may rise and so apparently increase the rubber-content of upper layers.

§ 54. Determination of the rubber-content of latex.

A determination of the rubber-content of latex is effected in practice for the following purposes:

1) control of the coolies, especially when they are paid by weight of rubber collected. The volume of latex that each coolie brings to the factory is weighed or measured, but the rubber-content must also be controlled to detect accidental or intentional addition of water.

2) to get an estimate of the total rubber to be expected from one day's production, calculated from the total volume of latex and its rubber-content. For this purpose, however, the wet weight of the rubber after it has been rolled forms a better gauge and is generally used.

3) to dilute the latex to a standard rubber-content and to determine the amount of chemicals to be used in coagulation.

§ 55. Trial coagulation.

The only sure way, known at present, to determine the rubber-content of latex, is actual coagulation of the latex

and weighing of the rubber. As it is generally desired to know the rubber-content immediately, there is no time to wait till the rubber is dry, and the dry weight is calculated from the wet weight.

Trial coagulation may be effected in any desired quantity of latex. Small quantities have the drawback that the unavoidable error is rather large, while large quantities give a loss in first latex rubber, as the crepe obtained from it (no bisulphite being used) generally is somewhat deficient in colour.

Used for the control of individual coolies, only small samples of latex (50 to 100 cc.) are taken, by small bamboo or zinc cylinders, which are filled to the brim by dipping them into the latex; the contents are poured into cups bearing the number of the coolie and coagulated with a few drops of acetic acid. After the bulk of the latex is received and coagulated, the small pieces of coagulum are creped in quick succession (catching them up in their own cup, as they emerge from between the rolls) and weighed wet, which gives sufficiently accurate data to fix the payment of the tappers and control the addition of water in the field.

For determining the rubber-content of mixed latex, generally 500 cc. or 1 liter are taken and coagulated by adding acetic acid in a proportion of approximately 1 part acid in 60 of rubber. Coagulation may be accelerated by stirring, and in 10 or 15 minutes the coagulum may be rolled. It is best to make thin crepe from it, which is shaken out and rolled up in a piece of cloth to remove surface-moisture. When care is taken to treat the little piece of crepe every day in a standard manner, the moisture-content of the wet thin crepe so obtained is very constant, but it has to be determined for every estate by preliminary experiments, once the method of preparation is fixed, because it depends upon the thickness of the crepe, the manner of surface-drying, etc. It generally lies between 7 and 20 %. For diluting the latex to the desired standard rubber-content, tables are then drawn up, giving the amount of water to be added, for instance, to every 100 liters of latex, for different wet weights of crepe from trial coagulation. For diluting the

latex to 15 % and for moisture-contents in the trial crepe of 15, 12 1/2, 10 and 7 1/2 %, figures may be found in the following table.

Weight of wet trial crepe from 100 cc. of latex, gms.	Liters of water to be added to 100 L. of latex when the moisture-content of the crepe is			
	15 %	12 1/2 %	10 %	7 1/2 %
45	155.1	162.5	170	177.4
44	149.5	156.7	164	171.2
43	143.8	150.9	158	165.1
42	138.2	145.1	152	158.9
41	132.5	139.2	146	152.7
40	126.8	133.4	140	146.6
39	121.1	127.6	134	140.4
38	115.4	121.7	128	134.3
37	109.8	115.9	122	128.1
36	104.1	110.1	116	122.0
35	98.4	104.2	110	115.8
34	92.8	98.4	104	109.6
33	87.1	92.5	98	103.4
32	81.4	86.7	92	97.3
31	75.7	80.9	86	91.2
30	70	75	80	85
29	64.3	69.2	74	78.8
28	58.6	63.3	68	72.7
27	52.9	57.5	62	66.6
26	47.3	51.7	56	60.4
25	41.6	45.8	50	54.2
24	35.9	40.0	44	48.1
23	30.2	34.1	38	41.9
22	24.6	28.3	32	35.7
21	18.9	22.5	26	29.5
20	13.3	16.7	20	23.4

An objection to the method of trial coagulation, viz. that a certain time has to elapse between the taking of the sample of latex and the rolling of the coagulum from it, may be overcome by taking the sample from the bulked latex, after a thorough stirring, when the larger part of the coolies have come in. For all practical purposes the rubber-content so found may be taken as equal to that of the final amount of latex.

J. C. HARTJENS, Arch. 1 (1917), 374.

For accurate determinations it should not be forgotten that the weight of rubber obtained depends upon the method of preparation. The differences in weight will be treated in § 128, 150 and 159; from them it will be seen that crepe from undiluted latex, rolled shortly after coagulation, is somewhat heavier (nearly 1 %) than crepe from 15 % latex, rolled the next day. In the same way trial coagulation was found to give 0.8 to 1.9 % more in weight than crepe from 15 % latex, whilst the difference with the weight of sheet was negligible.

O. DE VRIES, Arch. 3 (1919), 214.

This difference is too small to be of any significance in actual practice. The unavoidable errors in trial coagulation, and especially in determining the volume of latex, certainly exceed 1 %. In exact experiments, when indicating the rubber-content of latex, the method in which it is determined should always be accurately described.

§ 56. Use of densimeters.

Densimeters are also often used for the purposes just treated. It should however not be forgotten that they indicate the specific gravity of latex, and that a conclusion as to the rubber-content is only feasible when the relation between rubber-content and specific gravity is known and is constant.

We have treated this relation in § 15 and depicted it in Fig. 1, of which a part is reproduced on an enlarged scale in Fig. 4, the rubber-content being expressed in grams per 100 cc., and not in percentage of weight, to make it comparable with the densimeter-readings.

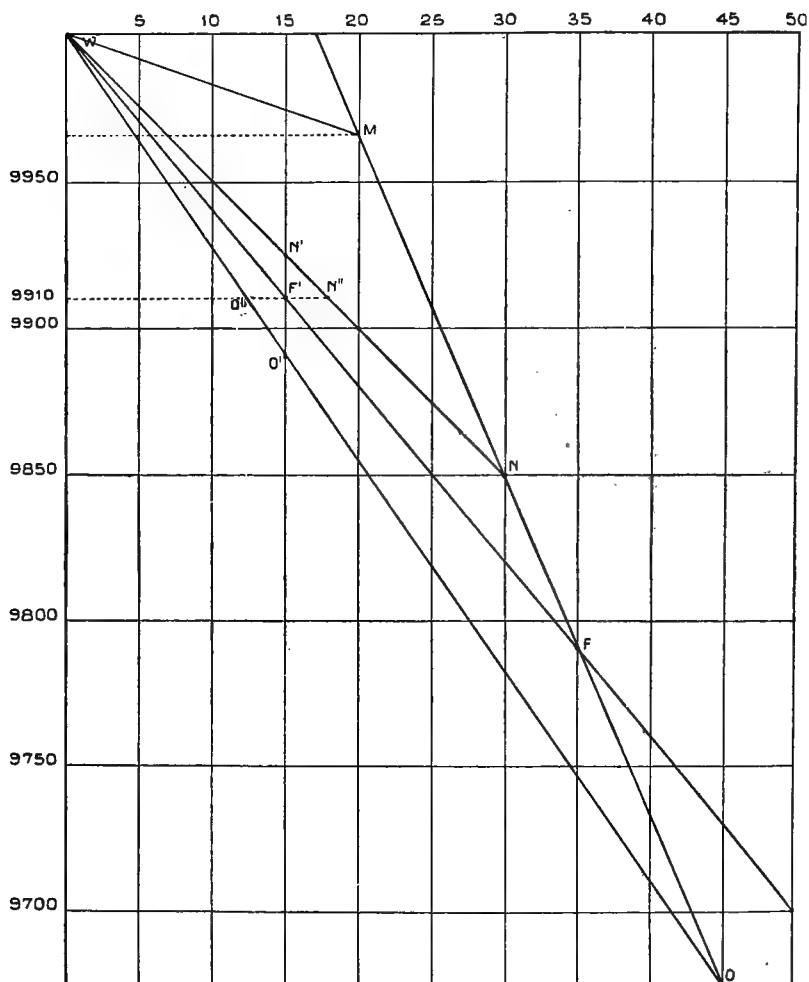


Fig. 4.

Specific gravity and rubber-content of latex (part of Fig. 1 on an enlarged scale; rubber-content expressed as gms. per 100 cc. latex).

§ 57. Specific gravity determinations in pure undiluted latex.

The values for rubber-content and specific gravity of undiluted latex range along the line OM (Fig. 1 and 4) or (when the composition of the serum changes) in a small area on either side of it (see § 15). It would be possible to construct a densimeter holding good for this relationship; but such an instrument would probably not serve any practical purpose. In the first place pure undiluted latex is mostly too viscous to allow densimeter-readings to be taken, at least in factory-practice; and further, latex is often diluted to some extent by water remaining in cups or pails, from wet trees, by solutions of anti-coagulants etc., for which cases the instrument would not hold good.

G. VERNET (C. Gp. 1910, 4549), as the result of a large series of experiments, gave a relation between rubber-content and specific gravity, represented by a curved line, which in Fig. 4 would lie somewhat to the right of OM. He designed a pykno-dilatometer especially fit for determining the specific gravity of latex. Working along these lines, L. SCHEIN (Bull. SAIGON I (1919), 340) with the product from a large estate where the latex is collected pure, i.e. without addition of water, found an excellent agreement between „weight calculated from specific gravity of undiluted latex” and „weight actually obtained” over several months; but, of course, in months when the latex was diluted by rain, the weight calculated from pyknometer-determinations was too high.

§ 58. Metrolac and Latexometer.

The instruments most generally in use bear the above names. The Metrolac has the advantage of a cigar-formed body, and moves more easily in the latex than the broad blunt Latexometer. In the latter changes in weight (caused, for instance, by wear) may be compensated by adding weight in the small bulb at the base, and the instrument may be adjusted easily by bringing the reading in pure water to exactly 1.0000 (to which point the stem of the Metrolac does not reach).

Both instruments have been constructed on the same scale; the Latexometer being graduated for specific gravity, whilst on the stem of the Metrolac the supposed rubber-content is indicated in pounds per gallon of latex. This scale is represented in Fig. 4 by the line WF, for which the following relation holds:

Rubber-content in % (gms per 100 cc.)	Specific gravity
5 %	0.9970
10 "	0.9940
15 "	0.9910
20 "	0.9880
25 "	0.9850
30 "	0.9820

and so on, 1 % rubber-content corresponding with 0.0006 in specific gravity.

The principle on which these instruments have been constructed is therefore that a certain latex, say F with 35 % rubber-content and 0.9790 specific gravity, represents the normal case, in which latex, when diluted with varying amounts of water, the instruments indicate correctly the rubber-content from specific gravity.

There are, however, as we have seen in § 14 and Chapter II, a large number of factors which affect the rubber-content of latex; and the rubber-content of original latex then follows the line OM, as long as changes in composition of the serum do not cause small deviations to the right or left of it. Now take a latex N with an original rubber-content of 30 % and a specific gravity of 0.9850, which may often be obtained with ordinary tapping systems. The instruments, used in such a latex, give the specific gravity rightly 0.9850, but from this a rubber-content of 25 % is estimated, or only 83 % of the real content. In a latex with a high rubber-content, such as O with 45 %, obtained, for instance, when tapping is started after a period of rest, the instruments correctly indicate the

specific gravity 0.9675, but transpose this to 54.2 % rubber-content, which is too high, 120 % of the real content. In latices with an abnormally low rubber-content, obtained by very heavy tapping, such as M with 20 % rubber, the instruments would indicate, from the specific gravity of 0.9966, that the rubber-content is only 5.5 %.

The further therefore the rubber-content of pure, original latex departs from that of F, which is chosen as the normal type in the construction of Metrolac and Latexometer, the larger the errors of the instruments will be. As long as latices which in composition differ only slightly from F have to be tested, the errors may be of no practical importance. It should not be forgotten that in an estate-factory the readings cannot be effected with the exactness of laboratory-work; and that in other determinations, such as the total volume of latex, rather large errors are unavoidable in practice, so that there is no sense in requiring a greater accuracy in the determinations of the rubber-content.

In actual practice, however, the rubber-content of the original latex is sometimes higher and often lower than that of F. Cases where the densimeters indicate only 70—80 % of the real rubber-content are quite common, whilst figures of only 60 and even 40 % have been found on estates in Java.

J. C. HARTJENS, Arch. 2 (1918), 273.

O. DE VRIES, Arch. 3 (1919), 218.

In cases where the original latex deviates from F, an instrument with a corrected scale, or with a table suited for the composition of the latex in question, might be used. But even then it should not be forgotten that there are many factors which change the rubber-content of original latex, for instance, the monsoon, a change in tapping system, etc. For all such cases new corrections would have to be made.

The use of densimeters to determine the rubber-content of latex is at best a compromise, of value only so long as the tree does not change the rubber-content of its original, undiluted latex.

§ 59. Use of densimeters to control the coolies.

The use of densimeters has some advantages in the control of the latex from individual coolies. In the first place a reading is obtained immediately, before the eyes of the coolie himself, and one has not to await the rolling and weighing of the coagulum. Further, no rubber is lost, or better it is not reduced to second quality.

But then it should not be forgotten that some fields may yield latex of lower rubber-content than others, and that, when the original rubber-content is lower than that of the latex-type, the densimeters give the rubber-content lower than it really is. To avoid injustice in payment of the coolies, this would have to be determined and controlled.

It may be added that the viscosity and colour of the latex, as judged by the trained eye from that adhering to a lead-pencil or a stick dipped in the latex, may allow a fairly accurate estimate of the degree of dilution, a rough method of judging sometimes used by factory assistants.

§ 60. Use of densimeters to dilute the latex to standard content.

Perhaps the most general use of densimeters is made in diluting the latex to standard content; either by taking a reading in the mixed latex — undiluted, or diluted 1:1 — and calculating the amount of water to be added, or by simply adding water and stirring, till the instrument floats to the desired depth.

From the above it will be clear that by this procedure the latex is diluted to a standard specific gravity, and not to a standard rubber-content. In so far as the composition of the original latex remains the same — and this, for bulked latex from large areas, will be the case at least over periods of several weeks or months — the product from day to day will, of course, be just as uniform as when a standard rubber-content is chosen.

For examples of latex rather constant in composition see, for instance, A. A. L. RUTGERS and J. G. J. A. MAAS, Arch. 1 (1917), 289, who found densimeter-readings in such cases just as useful as trial coagulation.

When the rubber-content of the original latex changes, the effect of "diluting to standard rubber-content" and "diluting to standard specific gravity" is different, as may easily be judged from Fig. 4. Take, for instance, latices O and N. Diluting with water means a displacement along a straight line in the direction of W, and when a dilution to 15 % rubber-content is effected, the points O' and N' will be reached; but when the dilution is to 0.9910 specific gravity, the points O'' and N'' will represent the final composition. A latex of high rubber-content, such as O with 45 % rubber, when brought to a standard specific gravity of 0.9910, will contain only $12\frac{1}{2}$ % rubber. A latex N with 30 % rubber will, by this procedure, be diluted to 18 %, and an original latex with $27\frac{1}{2}$ % (approximately the lowest figure obtained by tapping-systems now prevailing) will show a rubber-content of $20\frac{1}{2}$ %, when diluted to 0.9910. This means that diluting to standard specific gravity causes a rather large difference in rubber-content of the dilute latex.

The question now is: which procedure is best for actual estate-practice?

In rubber-preparation a constant rubber-content of the latex ensures uniform working-methods; the dose of acid, the hardness of the coagulum, the rate of drying and other details all depend, to a certain extent, on the rubber-content of the diluted latex. Using a standard specific gravity, which results in a rubber-content of the diluted latex ranging from $12\frac{1}{2}$ to 20 %, may give variability in this respect, and for uniformity of factory methods the standard rubber-content is certainly to be preferred.

A second point, which has to be taken into consideration, is the uniformity of the properties of the rubber. On this point our knowledge is still lacking; in how far constant rubber-content gives a more uniform rubber than constant specific gravity of latex, has not yet been ascertained experimentally. It may, however, be assumed that the rubber will be more uniform when a constant rubber-content of the diluted latex is adopted; because when working on a constant specific gravity, the dilution of the serum will vary over a wider range, which

results in a correspondingly larger difference in rate of cure.

When diluting to 15 % content, the serum of latex O with 45 % rubber will be diluted with 3.64 times its volume of water; the serum of latex N, with 30 % rubber-content, with 1.43 volumes of water. When diluting to 0.9910 specific gravity, the serum of O will be diluted with 4.73, the serum of N with only 0.95 volumes of water; the ratio is therefore nearly twice as large.

See further discussion on this point in § 66.

From this it will be clear that diluting to standard rubber-content is the most rational procedure to ensure uniform working methods and uniform properties of the rubber. In how far diluting to standard specific gravity can replace it, is wholly a question of the variations in rubber-content of the original latex. On certain estates, during certain periods, the latex may remain constant in composition, so that the result is the same with both procedures. Small deviations in composition of latex may be without practical significance, because the errors in diluting the latex and other manipulations are also unavoidably rather large in estate-work. In some circumstances the composition of the original latex may show larger variations; and it may vary considerably from field to field, or from estate to estate. In such cases an arrangement would have to be made by taking another specific gravity as standard, according to circumstances. That the use of densimeters must lead to such compromises, has been discussed in § 58.

§ 61. Purposes for which densimeter-readings are useful.

From § 15 and Chapter II it will be clear that the rubber-content of the original latex is a rather important figure, because to a certain degree it indicates how the tree reacts to the treatment to which it is subjected. Whether this will have any practical importance, i. e. whether the condition of the trees may be judged to some extent by the rubber-content of the latex, remains to be investigated. But it is worth while to draw attention to the fact that specific gravity,

determinations may be of aid in such questions. As long as pure, undiluted latex is available, a simple trial coagulation is enough to give us the rubber-content. But it has been repeatedly argued in this book that in practice there are many sources through which the latex may become diluted to a small and often to a large extent. When there is a possibility of the latex being diluted, a specific gravity determination *in addition to* a determination of the rubber-content by actual coagulation may be a means of learning something about the composition of the original latex. Take a diluted latex in which is found 15. % rubber and 0.9925 specific gravity: point N' is obtained for it in Fig. 4, and in tracing the line WN', it may be concluded that the original latex must have had a composition approximately that of N (dependent upon small changes in composition of the serum). By a closer study of Fig. 4 it will be clear that for diluted latices the figure: „rubbercontent found by Metrolac, expressed as percentage of the real rubber-content” may serve as an easy indication of the composition of the original latex; when it is lower than 100 %, the original latex lies higher than F in the direction of M; when this factor is higher than 100 %, the original latex deviates from F in the direction of O.

See also O. DE VRIES, Arch. 1 (1917), 273.

§ 62. Errors due to wear of the instrument and to differences in temperature of the latex.

When using densimeters it should not be forgotten that there are, besides faulty reading due to the stickiness or the clotting of the latex or to pieces of dirt or splashed up drops of latex on the instrument, some sources of errors which may cause rather large deviations.

In the first place, the Metrolac as well as the Latexometer wear off in use (cleaning etc.) and gradually lose part of the yellow metallic coating resulting in a loss in weight of the instrument, and therefore causing it to sink less deep in the liquid. Thus the specific gravity is read too high, or the rubber-content too low. For Metrolacs used some years in the laboratory (that is with adequate care)

the difference amounted to 0.0005 and 0.0026 in specific gravity, or 0.8 and 4.5 units in rubber-content. A Latexometer, in use for some 3 years on an estate, showed a loss in weight of no less than $2\frac{1}{2}$ gms.

See O. DE VRIES, Arch. 1 (1917), 244 and 274.

In the Latexometer this may be corrected by adding weight in the small hollow bulb; for the Metrolac weight has to be added in some way to the bulb or stem, or another division of the scale has to be taken for standard-dilution. The instruments, when in use, should be regularly tested and adjusted; for the Latexometer this can easily be done by taking a reading in clean water at the temperature for which the instrument has been graduated. The Metrolac (the stem of which does not reach to 1.0000 specific gravity) has to be tested in liquids lighter than water, for instance, mixtures of alcohol and water, or dilute latex.

In the second place the temperature of the latex to be tested may differ from the temperature for which the instrument has been adjusted ($85^{\circ}\text{ F} = 29.45^{\circ}\text{ C}$ for the Metrolac; $84^{\circ}\text{ F} = 28.9^{\circ}\text{ C}$ for the Latexometer). The coefficient of expansion of latex increases somewhat with the rubber-content; the correction in specific gravity for 1° C may be taken to be:

Specific gravity of latex: . . .	0.9950	0.9900	0.9850	0.9800	0.9750
Correction in specific gravity for 1° C : . . .	0.00030	0.00034	0.00038	0.00042	0.00046

See O. DE VRIES, Arch. 1 (1917), 247 and 2 (1918), 261;
A. A. L. RUTGERS and J. G. J. A. MAAS, Arch. 1 (1917), 295.

The temperature of 29° C , for which the instruments are constructed, is common for latex of low-lying estates, where temperatures of 30° C and higher may often be found; in higher elevations, as on so many estates in Java, temperatures

of 25—27° C are normal, and 23 or even 22° C no exception. When the temperature of the latex is not determined — and in practice this is never done, and no correction-table is added to the instruments — errors of 0.0010 in specific gravity or 1—2 in rubber-content may often be found, and an error of 3 units in rubber-content, that is an error of 10 % for a rubber-content of 30 %, and of 20 % for 15 % latex, is no exception. For temperatures lower than 29° C the instruments, of course, give too high a specific gravity, or too low a rubber-content.

The actual error in reading the instrument may be reduced to 0.0001 or 0.0002 in specific gravity by very careful working. The observations of native laboratory workmen or of experimentors not specially trained in this work with latex which is rather difficult to handle, fluctuate between 0.0010 or ca 2 units in rubber-content. In the rather rough work on estates, where there is no time for very careful observations, and where curdling of latex, drops on the stem of the instrument, etc., may have unexpected results, the error of reading is much larger.

Compare O. DE VRIES, Arch. 1 (1917), 244 and 274.

§ 63. Other methods of determining the rubber-content of latex.

As the rubber-content of latex is such an important point, it is not astonishing that several other ways have been tried to establish an easy determination of it.

In the first place the viscosity of latex, which, as we have seen in § 16, increases rapidly with the rubber-content, has been used as a means of determination. Trials have been made with this method by several investigators, even on a fairly large scale in practice, but no published results are available. It may be assumed that the delicate character of even the simplest type of viscosimeter will act as a drawback to its use in an estate-factory, whilst the errors will always be rather large, even when using ammonia, due to the tendency of latex to form small clots, as described

in § 16; so that for actual practice not much is expected of this method.

An instrument using the colour of very thin layers of latex as a criterion of its rubber-content has also been proposed, and may give satisfactory results when used for the type of latex for which it is constructed. But the colour of latices of different origin shows such wide variations ranging from bluish to yellowish white, that such an instrument is not generally applicable.

G. VAN ITERSSEN, Comm. Delft I, 16.

J. C. HARTJENS, Arch. 3 (1919), 103.

A nephelometric method — adding latex in drops to a certain quantity of water, until a certain degree of milkiness is reached — has also been tried, but the experiments do not seem to have led to practical results.

G. S. WHITBY, The prime technical plantation problems of the next decade, International Rubbercongress, Batavia 1914, page 23.

§ 64. Influence of dilution on the properties of the rubber.

In this paragraph we treat only of the dilution of latex with clean water, as it is (or ought to be) done in the factory. The influence of water mixed with the latex in the field was discussed in § 39.

Influence on the composition of the rubber.

Thinning the latex means that the caoutchouc globules are distributed in a more dilute serum. The rubber globules, on account of their colloidal character, may be supposed to hold absorbed a certain amount of serum-substances; and when the serum in which they float is diluted, they have to give up part of these absorbed substances, and consequently carry with them less of these substances when coagulation takes place. This changes the composition of the rubber.

For instance, the ash-content of crepe changes with dilution of the latex in the following way:

Rubber-content of latex	Ash in crepe
35 %	0.3 %
30 "	0.25 "
25 "	0.22 "
20 "	0.19 "
15 "	0.17 "
10 "	0.15 ⁵ "
5 "	0.14 "
2½ "	0.16 "
1 "	0.18 "

Therefore there is a decrease in ash for crepe from diluted latex, as was to be expected. However this decrease seems to change again into an increase with crepe from very diluted latex, an interesting phenomenon which deserves attention in relation to the change in rate of cure, soon to be discussed.

The acetone-extract does not seem to show a marked change when the latex is diluted, whilst the nitrogen-content of the rubber decreases somewhat.

That the rubber from diluted latex includes smaller quantities of serum-substances, is also apparent from the moisture-content of the air-dry crepe or sheet (indicating, as it were, its hygroscopicity), which in samples from dilute latex may diminish to $\frac{2}{3}$ the figure for rubber from undiluted latex, and even less.

B. J. EATON (Bull. F. M. S. No. 17 (1912), 51) in one experiment found a slight decrease in protein-content of the rubber (from 2.6 to 2.2 %) caused by diluting the latex up to thrice its original volume; resin and ash remained constant, whilst the moisture-content increased markedly. Definite conclusions were however not drawn, and the results differ somewhat from those mentioned above.

Several experiments made by L. E. CAMPBELL (Bull. Ceyl. No. 32 (1917), 1; Bull. Imp. Inst. 16 (1918), 417) gave the following average figures:

	Loss on washing the sheet	Composition of dry, creped sheet		
		Ash	resin	protein
Latex undiluted	0.57 %	0.28 %	2.46 %	2.24 %
" diluted to 2 vols	0.35 "	0.22 "	2.55 "	2.17 "
" " " 3 "	0.39 "	0.20 "	2.49 "	2.09 "
" " " 7—9 "	0.33 "	0.15 "	2.42 "	2.04 "

Therefore a distinct decrease in ash, a small decrease in protein and no marked difference in resin-content, whilst the moisture-content (loss on washing) of the unsmoked sheet diminished with the dilution of the latex.

Influence on the properties of the rubber.

On the properties of the rubber, dilution of the latex has the following effect.

Rubber-content of latex	Tensile strength	Time of cure	Slope	Viscosity
30 %	1.39	110	36	39
15 "	1.39	120	36	34½
10 "	1.39	125	36	33
5 "	1.38	130	36	32½
1 "	1.37	135	35.7	27

The tensile strength is not changed, unless the latex is thinned to an abnormal degree, for example to 2 % rubber-content and less. This does not occur in practice with ordinary latex, because of the extremely great volume which such great dilution would give if for no other reason; but in wash- and rinse-water this unusually low rubber-content may occur, as will be discussed in § 179.

Whether this decrease in tensile strength is a real deterioration in the rubber, or whether it is only caused by the slower rate of cure, and the longer time the rubber is exposed to the temperature of vulcanisation in our method of testing, was not determined. Taking into account the figures mentioned in § 204, the latter explanation seems the most probable, so that diluting the latex would not mean any decrease in real intrinsic strength of the rubber.

Dilution of the latex causes the rubber to vulcanise more slowly, which, at least for the greater part, must be attributed to the lower content of non-rubber substances, as will be shown at length in § 112.

The viscosity decreases also with dilution of the latex; the slope is unchanged or improves a little.

See O. DE VRIES, Arch. I (1917), 33.

In the experiments made by L. E. CAMPBELL (Bull. Ceyl. No. 32 (1917), 1; Bull. Imp. Inst. 16 (1918), 417) somewhat different results were obtained. Diluting the latex up to 7 or 9 times its original volume caused, as in our experiments, no change in tensile strength; but a difference in rate of cure could not be detected in the unsmoked sheet, whilst in an experiment in which crepe was prepared the dilution was found to retard the rate of cure. It remains to be seen in how far this may be due to the effect of drying, which in our experiments with crepe took 1—2 weeks, in CAMPBELL's experiments also 1 to 2 weeks for crepe, but 3—5 weeks for the unsmoked sheet and up to 8 weeks for the sheet from very dilute latex, so that in these cases maturing may have played a role, and may have neutralised the retardation in rate of cure.

B. J. EATON and J. GRANTHAM (J.S.Ch.I. 36 (1917), 1220; see also Bull. F.M.S. No. 27 (1918), 192) found a marked increase in time of cure when the latex was diluted, both in the case of crepe and sheet; whilst the effect was still greater when the coagulum was allowed to mature (compare § 108). The increase in time of cure for latex diluted appr. from 21 % to 10 % was 10 % for crepe and 20 % for sheet; when the latex was diluted, appr. from 28 % to 14 %, the increase was 16 % for crepe and 30 % for sheet. The tensile strength in both cases on the average showed a decrease following dilution.

It may be mentioned that the decrease in rate of cure does not seem to continue for very large dilutions ($\frac{1}{2}$ % rubber content and less). In some of our experiments we found the crepe from $\frac{1}{2}$ % latex to cure even somewhat quicker than that from 1 % or $2\frac{1}{2}$ % latex, but in how far a change in composition (see above for ash-content), or the slower rate of drying (beginning of maturation) play a role, remains to be investigated.

Though dilution of the latex therefore has a distinct influence on the properties of the rubber, the effect on quality (tensile strength and slope) is negligible; and there is certainly no ground for the belief that rubber from diluted

latex is inferior, provided it was diluted with clean and not with dirty water. On the contrary, the intrinsic properties seem to remain unchanged by dilution.

The rate of cure diminishes somewhat, but the difference between 30 % and 15 % or even 10 % latex does not exceed the limits of ordinary variation in plantation-rubber. When the view is taken that every increase in rate of cure, even by 5 or 10 minutes, is an advantage, then diluting the latex from 30 % to 15 % would mean a decline in properties. When however uniformity in the product is of more importance, diluting the latex to a fixed standard is to be recommended. This will be discussed in the following paragraphs.

What the substance is, which causes the change in rate of vulcanisation, is as yet unknown.

Influence on weight of rubber.

As we have already said, the rubber from diluted latex carries with it smaller amounts of non-rubber substances than that from undiluted latex. This gives also a slight difference in weight, as an advantage for rubber from undiluted latex.

In crepe this difference is $\frac{1}{4}$ % to $\frac{3}{4}$ % of the dry rubber, in sheet it is about the same, although under some conditions it may reach 1 %. In the methods generally in use the difference is however of no practical importance and forms only a minor motive in the choice of a method of preparation.

Compare O. DE VRIES and H. J. HELLENDORF, Arch 2 (1918), 393.

Influence on other properties.

Dilution of the latex changes its colour gradually from yellowish to bluish tints; a slight difference, but tints ranging from yellowish to grayish, may sometimes also be noted in the crepe.

The influence of dilution on the viscosity of latex is of practical importance, and especially affects the ease with which latex passes the sieves, and with which the acid for coagulation is stirred in (see § 39 and 83).

The changes in specific gravity on diluting the latex and

their relation to the rubber-content were treated in § 15.

On the rate of coagulation and on the consistency of the coagulum the dilution of the latex has a great influence (see § 74 and 83). The coagulum from dilute latex is surely weaker than that from latex of high rubber-content; it is formed more slowly, and when taken from the latex encloses much more of the (dilute) serum, so that it is heavy and not compact, and, when sheeted and hung to dry may stretch considerably. But this does not mean that, after the serum has dripped out and the moisture is evaporated, the contracted air-dry rubber will be less strong.

Whether there is any real difference in structure of coagulum and dry rubber from undiluted and diluted latex, remains to be investigated; that an influence on the tensile strength, after the drastic reconstruction during vulcanisation, is not to be found, has been mentioned above.

§ 65. Why dilute the latex ?

From the foregoing it will be seen that diluting the latex, though it certainly does not have the deleterious effect on the rubber which it is sometimes supposed to have, causes a small decrease in rate of cure and viscosity.

The question may therefore arise: why dilute the latex at all? We have already mentioned in § 39 that in former years water was lavishly used in the field; latex with only 8% or even only 5% of rubber was no exception. These methods now have been abandoned; but still the latex is generally diluted to some extent in the field, in the rainy season, by wet tree trunks and wet surroundings in general, and further because cups and pails are, in practice, seldom completely dry.

Whilst therefore absolutely undiluted latex is obtainable only with the exercise of special care, many managers are not disinclined to see the latex diluted to some extent, because this facilitates handling (straining, etc.) of the otherwise rather troublesome viscous liquid.

For crepe-rubber further arguments are: to obtain a uniform dilution even on days when the latex is somewhat diluted

by rain; and to obtain a not too hard coagulum, so as to spare the rolls. For sheet-rubber the arguments for diluting the latex are stronger; as will be shown in § 66 and 68, they make the use of undiluted latex possible only in special circumstances.

Further it should not be forgotten that the addition of some water is unavoidable when an anti-coagulant or bisulphite is used, or even when the coagulant is being added.

It will therefore be clear that dilution of the latex to some degree lies along the line of the least resistance. Though the general trend now-a-days is to restrict the use of water in the field as much as possible, to prevent lump-formation and contamination with dirt, it is only the enthusiasm of some, in our eyes somewhat misplaced, for the superiority of rubber from undiluted latex, or the necessity of having the latex undiluted in processes such as spontaneous coagulation, that overcomes the practical difficulties of getting latex that is undiluted, or correctly speaking, diluted only to a small extent.

§ 66. Why dilute the latex to standard rubber-content?

Working with latex of standard content has the advantage, in practice, that one can give one prescription for the use of chemicals (acetic acid, etc.) without the necessity of calculating the dose each day. A further advantage is that the latex always coagulates with the same speed and that the coagulum is always of the same hardness, that the milling always goes regularly and in the same way, that the rubber dries at the same rate, and the colour is even; in short, that one gets a standardised and therefore, especially for large productions, a quick and cheap method of work.

In sheet-rubber especially is this a necessity, and it was already realised long ago that sheets „equal in weight, in size, and in thickness” were the first condition for well conducted manufacture. But in crepe-rubber also working with standard rubber-content deserves to be recommended: in addition to the greater uniformity in inner qualities (to be discussed further on), the external appearance is also

improved, because the colour of crepe depends to a certain extent on the dilution of the latex, and the effect of chemicals, such as bisulphite, in a latex of standard dilution will be the same from day to day. Many a manager has found with astonishment and pleasure a saving in cost of sorting the crepe, after working with latex of standard content. That in sheet-rubber the colour, the drying and the smoking are still much more dependent on the hardness of the coagulum, on the thickness of the sheets, and in short on regularity in working, needs no demonstration. Indeed, in general, it is very apparent that in rubber, which becomes more and more a mass-product, standardisation of preparation is a necessity.

These arguments, all bearing upon a regular course of preparation and a uniform outer appearance, are strong enough to emphasize the necessity of a standard dilution. Another important point is the uniformity in inner properties.

Although from the table on page 124 it will be sufficiently clear what variations in inner properties one may expect from latex of varying dilutions, we will give here a few examples to show its effect on the uniformity of the product.

In the first place we mention a case where an estate sent in samples from six different plots and from two successive days. The latex was treated in the old fashioned manner, that is, not mixed and not brought to standard dilution. The figures were:

Plot	Time of cure		Viscosity	
	first day	second day	first day	second day
1	150	> 140	28	31
2	> 140	130	30½	31½
3	> 140	> 140	30	34
4	135	125	30	31½
5	140	> 125	24½	28½
6	> 140	> 130	28½	30

Whilst the figures in the vertical rows give the variation caused by not mixing the latex, a comparison of the first and second day gives a good impression of the consequences of not diluting to standard-content. On the first day the latex was somewhat diluted by rain during tapping, and the average rubber-content for the whole estate fell to 21 %, whilst on the second day it was 30 %. The rate of cure is slower, and the viscosity lower, for nearly all plots on the first day.

O. DE VRIES, Arch. 1 (1917), 32 and 34.

The following table contains data for two estates preparing crepe, of which we regularly tested the product.

Estate	Method of work	Standard time of cure		Viscosity	
		Average	Extremes	Average	Extremes
I	(a) 5 months without standard-content	109 ± 5	100 — 115	1.83 ± 0.05	1.77 — 1.90
	(b) 6 months with standard-content	125 ± 2	120 — 130	1.73 ± 0.06	1.63 — 1.82
	(c) 10 months with standard-content	122 ± 2½	115 — 125	1.68 ± 0.03	1.55 — 1.74
II	(a) 5 months without standard-content	112 ± 6	100 — 130	1.81 ± 0.09	1.67 — 2.03
	(b) 5 months with standard-content	127 ± 3	120 — 135	1.74 ± 0.04	1.66 — 1.80

Compare O. DE VRIES and W. SPOON, Arch. 3 (1919), 258.

The average time of cure, after the application of the method of standard dilution, has become 15 minutes greater in both cases, in complete conformity with § 64; but the fluctuations (mean deviations from the mean) are reduced to half their former value, and also the extremes lie only

half so far from each other. The mean for the viscosity (here expressed as viscosity index, see Chapter XX) has decreased by 0.07—0.15, and the fluctuations (except in *lb*) are reduced to half, although large deviations (as the sample with 1.55 in *lc*) sometimes appear.

These figures give a good example of what is ordinarily gained by bringing the latex to standard-content; everything depends, naturally, on how exact the execution is, and certainly, with more careful work, even greater uniformity might be secured than is shown above.

For long series of samples, prepared according to standard methods in the laboratory or on an estate by a trained native assistant, the deviation from the mean was seldom more than 5 minutes in time of cure, and 3 units in viscosity.

§ 67. Influence of degree of dilution on uniformity.

For „uniformity” we have to distinguish two points, viz:

- 1) Uniformity in the product of a given estate from day to day;
- 2) Uniformity of plantation-rubber in general, i. e. from different estates.

That working on a standard dilution is to be recommended to ensure regular work in the factory, and that it greatly furthers the uniformity of the product of one individual estate, in outer and inner properties, has been shown in the foregoing paragraph.

In so far as the latex remains fairly constant in composition — and this will often be the case for plots or estates in regular tapping—the uniformity of rubber from undiluted and 15 % latex will be the same. As an example we quote the figures for standard time of cure for the plot already mentioned several times (§ 14, 20):

	Crepe from undiluted latex, rolled same day	Crepe from 15% latex, rolled same day	Crepe from 15% latex, rolled next day
May 1919. . . .	110	—	115
June	112	124	119
July	112	123	115
August	113	125	114
September . . .	110	123	112
October	110	120	110
November . . .	106	120	114
December . . .	107	120	116
January 1920. .	109	120	116
February . . .	107	120	115
March	109	119	116 ⁵
Average	109 ⁵	121 ⁵	115
Average deviation from the average	2,0	1,9	1,6

The variations from month to month, and the average deviations from the general mean, are practically the same for the three methods of preparation, as was to be expected for latex of constant composition.

The question, now to be answered, is: which standard dilution gives the greatest guarantee of uniformity for plantation-rubber in general?

In the time that restricting the dilution of latex within reasonable limits, and standardise it, was the next aim of those who had to advise the planting community, a dilution of 15% was chosen as a suitable figure that could be reached on every estate and needed only to be surpassed on very rainy days, on which the latex was also contaminated with dirt, bark-extract etc., and the rubber unavoidably somewhat inferior in colour and properties, so that it had to be kept separate for several reasons. At the same time it was, however, hoped that the general use of 15% as a standard dilution would insure uniformity in the product of all estates. That this is not the case, was shown in § 37

and is apparent from Fig. 2; and the reason of it was exposed in Chapter II, namely, that the composition of the latex undergoes changes by so many factors that cannot be regulated at will.

The question now is: would not the choice of undiluted latex as a standard ensure greater uniformity in the product? In Chapter I and II we have seen, and in § 111 it will be discussed further, that the composition of the serum changes; and as long as the substance or substances that cause the variations in rate of cure are not yet known qualitatively and quantitatively in all circumstances, an exact answer to this question is not possible. But the probability is great, that undiluted serum from trees under different circumstances will differ less in composition than the diluted serum of latices brought to 15 % rubber-content.

In extreme cases we found the specific gravity of original serum to vary for instance from 1.0195 to 1.0173, the total solids from 4.84 to 3.87, and the ash from 0.59 to 0.81 (see § 29). The extremes contained 40.6 and 19.3 % rubber.

Now, a latex with 40.6 % rubber-content contains 59.4 parts of serum; to bring this latex to a rubber-content of 15 %, $\frac{40.6 - 15}{15} \cdot 100 = 170\frac{1}{2}$ parts of water will have to be added, and the 59.4 parts of serum will therefore be diluted with $\frac{170\frac{1}{2}}{59.4} = 2.9$ volumes of water.

In the same way, when bringing a latex of 19.3 % rubber-content to 15 %, the serum will be diluted with $\frac{(19.3 - 15)}{15} \cdot 100$

or only 0.35 volumes of water. The specific gravities of the diluted serum in the 15 % latices will have become 1.0050 and 1.0128, the dry substance 1.24 and 2.86 and the ash 0.15 and 0.60 %. The differences, especially the relative values, are therefore greater, and it is probable (though not yet certain) that, taken in general, undiluted latices will give a more uniform product.

For tapping trees that had a rest, in which case the above factor (the difference in rubber-content) comes into the field very markedly, this may be shown by the following figures. The time of cure for crepe from undiluted and 15 % latex, (both rolled some hours after coagulation) was:

	Crepe from undiluted latex	Crepe from 15 % latex
1st day	130	160
10th „	125	145
23rd „	> 115	125
28th „	115	> 115
6.— 8th week	110	116

The range of variation for the crepe from undiluted latex was therefore less than half that for crepe from 15 % latex (20 against 44 minutes).

Whether in other cases, where the composition of the latex undergoes changes, the undiluted original sera also show less differences in composition than the diluted sera of latices brought to standard content, remains to be investigated, and can only be definitely solved when the vulcanisation-catalysts in the serum are known. In the mean time a large experimental material might decide whether rubber from undiluted latex, or from latex as little diluted as is possible in actual estate-practice, shows a greater uniformity than when working to a standard dilution. Sufficient reliable data are not yet available; but the probability is great, that working with latex as little diluted as possible would limit the range of variability, especially in extreme circumstances when the rubber-content of latex is abnormally high or low.

Changes in composition (dilution) of the serum, when bringing the latex to a standard rubber-content, might for the greater part be overcome by using, instead of water, serum of the foregoing day to dilute the latex. This has been often tried to spare acetic acid (see § 85 and 114); we will treat the effect of diluting with serum in § 112, where it will be shown that diluting the latex with fresh serum leaves the time of cure unchanged, when the coagulum is milled some hours after coagulation.

It would even be possible, by adding serum and water, to bring the latex in all circumstances as well to a fixed

rubber-content, as to a fixed dilution (content of non-rubber substances) of the serum; but such a procedure, which involves rather complicated calculations, and to the adoption of which the demands of market or manufacturers do not lend support, has, at least furtherhand, only theoretical importance.

§ 68. Standard dilution to be chosen for sheet-rubber.

On the ground of long experience 15 % dry rubber is recommended by the Experimental Stations as the standard content in the preparation of sheet-rubber. This rubber-content gives a coagulum which is not too hard and not too soft, easy to mill without danger of tearing or of stretching too much when hung to dry. The coagulation also does not proceed too rapidly, latex and acetic acid are easy to mix, and there is thus less chance of troubles such as air-bubbles etc.

These are therefore practical reasons, tending to assure a sheet of good and uniform outer appearance; and the demand for a faultless exterior is so paramount — the risk to fetch a lower price by any deficiency in this respect so great — that, for the preparation of sheet-rubber, diluting the latex to 15 % is now the general custom.

Some estates perhaps use a still larger dilution, say 12.5 %, by which the coagulum is somewhat weaker and may in certain circumstances be easier to handle and mill.

See, for instance, G. S. WHITBY, J. S. Ch. I. 35 (1916), 494.

Other estates use or have used a more concentrated latex, of 20 or 25 % rubber-content, or even so-called undiluted latex; and when local circumstances (for instance, time between tapping and coagulation; rapidity by which natural acidity develops in the latex; rubber-content and viscosity of the original latex) are favourable, a good product may be obtained. But often in the long run there comes a time when the undiluted latex gives trouble, and the sure way, diluting to 15 %, is then mostly reverted to.

§ 69. Standard dilution to be chosen for crepe-rubber.

For crepe-rubber the arguments relating to the exterior do not point so decidedly in the direction of diluted latex. Whilst the use of a standard dilution is just as imperative as in the preparation of sheet — uniformity in addition of chemicals, in progress of coagulation, in milling and drying, in colour and appearance of the finished product — the arguments for different standards are nearly at par.

Coagulum from diluted latex (say 15 %) is weaker, easier to mill, especially in the first roller, and gives therefore less wear of the rolls; the latex can be brought to standard rubber-content also on days that the trees are wet or that a beginning of rain interferes with the tapping.

Coagulum from concentrated latex is hard to cut and to mill, especially when it is left overnight and treated only the next day; on wet days the latex may be diluted below standard. On the other hand, for concentrated latex the total volume is less and the mixing tank may be smaller; the amount of acetic acid may be somewhat less (see § 83), the weight of the dry crepe is somewhat increased (see § 128), the rate of cure of the crepe is greater (§ 64) and probably the product of different estates, and of one estate under different circumstances, will be more uniform (see § 67).

Though the arguments are not decisive in either sense, the use of concentrated latex has advantages as long as the mills are strong enough to work the coagulum with ease. A further practical argument may be that on some estates the supply of clean water to dilute the latex is rather short.

Many estates prefer to dilute the latex to 15 % either because the latex comes from the field in a somewhat diluted state, or because the coagulum will be less hard on the following day and easier and quicker to mill. As a general rule, it might be recommended to choose the standard content as high as compatible with the circumstances on the estate; 20 % and even 25 % will often give very satisfactory results.

Of course, „undiluted” latex might also be chosen as the standard; and on estates where circumstances allow to get

the latex to the factory in a really undiluted state, this would in many respects be preferable (see § 67). Often, however, the „undiluted” latex is in reality diluted to some extent, and using it without further dilution would then simply mean shunning the difficulty of determining the rubber-content and bringing the latex to standard-dilution. Certainly, the „undiluted” latex may be very constant in rubber-content over a period of days and weeks; but gradually or unexpectedly the coolies may change their routine and add more or less water; and on wet days the rubber-content should in all cases be determined.

§ 70. Dilution of latex with wash-water or serum.

When pure water is used in the factory for rinsing, and washings which do not contain dirt are thereby secured, one can safely use this for diluting the latex, in which case the rests of latex collected by rinsing are not lost or incorporated in the lower grades. We will take this up again in § 179; here we only wish to emphasize the more theoretical point, that one must not think that the rubber-globules in wash-water and in extremely dilute serum have become irreparably inferior. They show an inferior quality only when coagulated (often better described as flocculated) from this extreme dilution. If these rubber-globules are brought into a less dilute medium, by mixing the wash-water with concentrated latex, then the properties after coagulation become normal, and there need be no fear that the rubber from normal latex will be mixed with less valuable rubber through diluting with very dilute latex. Provided, naturally, one mixes no dirt or contamination into the latex; and this, in practice, generally draws a very narrow limit to the use of wash-waters for diluting the latex, as the rinsings from cups or pails, and even from tanks and jars, often contain the collected dirt and sediments. However, when clean water is scarce, the point may deserve attention.

Another expedient in such a case is the use of serum of the foregoing day, which we treat in § 85 and 114.

CHAPTER V.

COAGULATION.

§ 71. Study of coagulation.

For estate-practice coagulation means the obtaining of a coherent clot of a hardness and consistency suitable for working in the proper manner. When the usual prescriptions are followed, this is easily obtained under all circumstances, and coagulation with acetic acid may now be said to present no practical difficulties.

Though the practical side of the question may therefore be regarded as settled, the process and mechanism of coagulation are far from sufficiently explained. Whilst this is not of interest to the practical man, who obtains his clot without trouble, the theory of coagulation, apart from its scientific value as applying to an important and special type of colloid, is needed as a base for a rational system of preparation. In our present ignorance with regard to the matter of serum-substances and the way they are affected by coagulation, the effect of different methods of coagulation can only be judged by practical results — which is a long and difficult way, if not illuminated by the light of theoretical considerations. Ultimately, only a better knowledge of the whole process of coagulation can determine which method of preparation is the best.

Several things have hampered the progress of our knowledge on this point. The first is, that the opinions of different authors on coagulation have mostly been founded on one special type of latex, or on one type of coagulation. A theory built up for a resin-rich latex as *Funtumia*, *Castilloa* or *Ficus* need not hold good for a latex poor in resins as

Hevea. At the same time, coagulation in one and the same latex, complicated as this fluid is, need not in all cases be caused by the same phenomenon, or proceed along the same lines.

A second point, which is often neglected in critical studies, is that coagulation in Hevea-latex is different from other processes in which the phases of an emulsion or suspension are separated; then again in coagulation, after the separation proper, a second and special reaction takes place in the formation of a coherent clot, which differs from, or at least shows a much more marked coherence than, an ordinary gel, and is totally different from the precipitate from suspensions such as clay or others, which separate out as powders.

Further the condition of the latex to be investigated is a point that may cause confusion. Latex preserved with ammonia or formalin and investigated in Europe may show phenomena other than those of fresh latex in the East. Fresh latex increases in acidity on standing, whilst serum-substances are decomposed, which factors also should be taken into account. Further the dilution of the latex plays an important role. The influence of these factors on coagulation is so large, that a great many of the results obtained in Europe, and of the conclusions arrived at, do not hold for fresh latex in the East. As a large part of the investigations done in the East have been made with diluted latex, the actual state of affairs is that on the coagulation of fresh, undiluted latex our knowledge is indeed rather scarce — that is to say, of course, concerning processes other than those in general use on estates, which we will treat in Chapter VI.

Therefore, generalisations should never be made from the conclusions and facts discussed in this chapter, but these should be taken with the restrictions given for them; we will have to state repeatedly that data found in literature do not hold good for undialysed, or for undiluted latex.

In reviewing the data mentioned in this chapter it may be stated that coagulation under different circumstances is still far from explained. The different forms of curdling, clotting and partial coagulation, occurring in actual practice,

and the action of anti-coagulants to prevent them, still need much further study. The course of coagulation by acids should be investigated and described more explicitly, working out quantitatively the influence of dilution and amount of acid, and distinguishing between the arresting of the Brownian movement, the separation or precipitation of the rubber globules, and the formation of a coherent clot or coagulum. The role and behaviour of the proteins under different circumstances should be fixed by well-founded facts. The question, whether or not enzymes play a role under certain circumstances, is not yet settled. Fresh, and especially undiluted, latex has been somewhat neglected in the researches done up till now. Dialysed latex, which forms such an important point of attack, should however not be left out of consideration. Recent investigations on the flocculation of other colloids, especially proteins, may of course help greatly in clearing up the phenomena of latex-coagulation.

§ 72. Different methods of coagulation.

Separation of the rubber-globules in latex may be obtained by very different methods, of which the principal are:

- 1) by mechanical means,
- 2) by physical means,
- 3) by chemical means.

Separation by mechanical means succeeds in many latices, for instance, in *Ficus* latex by stirring (churning). Centrifuging also often gives an easy separation, for instance in *Castilloa*-latex. *Hevea*-latex however does not readily yield all its rubber on mechanical treatment as long as it is unchanged, though by churning, shaking and so on, part of the rubber may be made to clot together, especially if the latex has developed natural acidity. When flocks have formed in some way, these may of course be separated mechanically (compare § 18 and 103). Latex, which has developed natural acidity, may of course react in a different manner, and centrifugation in a slightly acidified latex is possible. Latex from trees which were given a rest, with its high rubber-content, is more

easily subject to all means of separation than ordinary, less concentrated latex. A partial clotting in ordinary latex, with its natural acidity, by slow stirring, was for a long time used as a method of „purification”, see § 176 on partial coagulation.

Physical treatment may give a separation of rubber in Hevea-latex. The effect of heating we will treat in § 100, of freezing in § 101. Rubber obtained by evaporation will be treated in § 102, whilst the influence of an electrical current is discussed in § 194. Of course, these physical treatments, in so complex a fluid as latex, may be accompanied by some chemical reaction between its own constituents, so that the phenomena, in detail, need not be purely physical.

One of the simplest chemical means, diluting the latex with water, gives an easy separation, for instance, in *Castilloa*-latex; for which this is one of the ordinary procedures; water-soluble substances, which seem to act as emulsifiers, are probably washed out. Hevea-latex, however, does not yield rubber on dilution; in very diluted latices it is even difficult to separate the rubber by the addition of acids:

The number of chemicals that cause coagulation is very large. We will treat the practical aspects of these processes, amongst which natural or spontaneous coagulation is also to be reckoned, in Chapter VI, and discuss the action of some of them, especially the acids, in the following paragraphs.

§ 73. Forms of separation.

Rubber can be separated from latex in different forms, such as flocks, clots, lumps etc.; in practice however the end is always a coherent clot. Different names, such as flocculation, aggregation, agglutination, coalition, coalescence, have been given to these processes by various authors, but these words are used in different senses and no exact

definition of them is universally recognised, so that confusion often arises from their use.

We will here simply describe some of the more important phenomena, using plain English names.

1) *Creaming.*

Under special conditions a separation of the rubber-globules from latex may be obtained, which is reversible, that is: by changing the conditions, the globules go into suspension again, and a latex-like fluid is again formed. The globules are separated in a cream- or flour-like condition and do not unite.

This creaming is easily obtained in latices such as *Castilloa*, where simple dilution causes the fluid to cream; but in Hevea-latex it is seldom met with.

V. HENRI (C. Gp. 1908, page 2409) describes such a form of separation by the addition of salts of bivalent or trivalent metals to a strongly alkaline latex, and calls it agglutination. Small particles are separated, which on shaking are suspended again in the liquid. It would seem, however, that in this case some kind of change has already taken place, and that the re-suspended particles are not the same as the original rubber-globules.

The word „creaming” is used by CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 35; also Z. Koll. 13 (1913), 217) for a separation of aggregates, for example, in normal latex to which insufficient acid has been added. The aggregates do not unite and can be distributed again by vigorous shaking, so that the liquid again looks like normal latex. This would, however, seem to be a separation somewhat advanced in the direction of curdling (see below). Of course, all kinds of transitions occur, and no sharp limits can be drawn,

L. E. CAMPBELL (Trop. Agric. 45 (1915), 231) calls creaming the thickening of the latex in the early stages of slow coagulation, in which it becomes of a creamy consistency without losing its fluidity. Generally this is followed by the formation of minute floccules, which increase in size and gradually unite.

2) *Curdling and flocking.*

Smaller or larger flocks are formed in the latex, which for a long time do not unite, but float separately in the milky fluid. This is very common for instance on rainy

days, when the latex, though fluid, may contain numerous small flocks. When collected on the sieve, they readily cohere; but many of them may be so small that they pass through the sieves.

Another form of curdling may be obtained when an excess of strong acid is added to concentrated latex, for instance, in trial coagulation. The latex soon changes into a mass with a porridge-like consistency, which on standing unites to one coherent clot, but which when diluted may change into separate clots, which are not so easily brought together. Care is therefore necessary in trial coagulation so as not to use an excess of acid, in which case the obtaining of a workable clot is retarded, unless the formation of a coherent clot is quickened by stirring.

A flocky precipitate is also obtained when acid is added to very dilute latex, for instance, that secured by washing the pails, cups etc. The rubber soon rises, but the flocks are so weak that it is often not easy to knead them into a coherent clot, though, as in all cases, this is the final stage reached after a sufficient length of time.

Further, when coagulation is effected with some salts such as sodium sulphate (which then have to be used in large quantities, see § 89), a flocky precipitate may be obtained, which only gradually unites into a coherent clot.

Similar flocks are formed in the long run in latex when it is preserved with formalin, see the description and figures by CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 18; also Z. Koll. 13 (1913), 208), who call this aggregation. Curdling or flocculation was described by them for formalin-preserved latex as occurring on the addition of not too large proportions of acid (say 0.15 %); and for latex containing salts (for instance, 2 % or 3 % ammonium sulphate) when acetic acid is added in amounts equal to 0.05 % to 2.5 %.

The size of the aggregates was found to increase with increasing amounts of coagulant.

Flocking or flocculence is described by L. E. CAMPBELL (Trop. Agric. 45 (1915), 231) for latex to which much formalin has been added. Small particles of rubber are formed without coalescence of the same to form lumps.

3) *Clotting or lumping.*

The latex in practice may also form larger clots or lumps which are distinct from the minute flocks described above.

Often these originate from separate cups, in which latex has coagulated, partly or wholly, by evaporation on the walls of the cup or on the surface of the latex, or from other causes (see § 177). This coagulum from a separate tree may however grow in the latex to a large spongy mass.

Of course, the delimitation from the former group is not sharp. For instance, on rainy days the latex as a whole may curdle somewhat, showing very fine flocks; but the latex of some coolies may have changed to a mush-like mass of separate spongy clots, from which a quantity of fluid can be pressed through the sieves, while the rest, when rubbed on the sieve, sticks together and forms one large clot.

Partial coagulation by small amounts of acid (see § 176) also generally results in the formation of clots, but here stirring plays a role in uniting the particles that separate. Adding a coagulant without sufficient stirring (so that it is locally in excess) may cause the formation of a clot, which may be regarded as a local coagulation in the place where the coagulant enters the latex; and the same takes place when a coagulant is used which causes immediate coagulation, such as alcohol.

Though, of course, the different forms of separation show many transitions, clotting may generally be regarded as due to some kind of local or partial coagulation; it does not constitute such a distinct form of separation as creaming or curdling.

4) *Coagulation or congealing.*

This is the form that is aimed at in practice; the rubber separates in one coherent mass, which at first fills up the whole volume of the latex, but gradually contracts, leaving a clear serum.

In the ordinary course of coagulation the liquid mostly passes through a stage of curdling or porridge-formation, a separating into numerous small flocks, which then unite; but this is of no importance in practice, where the mass is simply left undisturbed till a sufficiently hard coagulum is formed. In rapid coagulation in a concentrated latex, the

formation of a coagulum may proceed so quickly that a transitory flocking can hardly be observed.

As has already been stated above, the tendency of the rubber-particles to cohere is so great that all forms of separation end in the formation of a coherent clot, and a powdery form of precipitate in a dry state is not obtained.

V. HENRI (C. Gp. 1906, 513) especially emphasised the fact that there is a gradual transition from agglutination (flocking) to coagulation, so that coagulation proper is closely connected with other forms of flocking or precipitation of colloids.

§ 74. Course of coagulation.

The first stage of coagulation consists in a stagnation of the Brownian movement of the rubber globules (§ 1), which then clot together. This can be followed very distinctly under the microscope.

See description and figures by V. HENRI (C. Gp. 1908, 2405, reviewed in Lectures 1908, 203) who followed coagulation cinematographically; further the illustrated descriptions of CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 24; also Z. Koll. 13 (1913), 211).

Apart from the varying ways of separation treated in the foregoing paragraph, the course of ordinary coagulation may differ considerably. The principal factors are: the dilution, and the quantity of acid. In treating this subject it should always be borne in mind that the decisive dilution is the final dilution of the fluid set to coagulate, that is the mixture of latex, water and (dilute) acid. The greater the rubber content of the final mixture, the quicker a coagulum is formed; the more dilute it is, the longer it takes to obtain a coagulum, the weaker this coagulum is, and the more it contracts on standing.

Acetic acid coagulation, by far the most important in actual practice, is a slow and continuous process, which may take from $\frac{1}{4}$ to 6 or 10 hours. The rate of coagulation can be easily regulated by changing the ratio of latex, water

and acid, so that a coagulum of the desired hardness may be obtained at the time when it has to be rolled.

Influence of quantity of acid.

The less acid one adds to a certain latex, the slower coagulation proceeds; but this holds only within certain limits. Too little acid gives incomplete coagulation, the serum remains milky and may contain rubber (see § 115). By increasing the amount of acid, a limit is also reached, the latex solidifies quickly, but forms a porridge (see § 73) which only slowly coheres to a clot. By larger doses of acid, coagulation may even be completely prevented. With acetic acid, the range of doses which give a good coagulation is much larger than with some mineral acids, but the proportions vary with the dilution of the latex, the temperature, and the other substances present, especially the salts.

With some acids, the region in which no coagulation is effected is also limited. Small amounts produce coagulation; larger amounts give partial coagulation or none, and still larger amounts of acid again produce coagulation or flocking; so that, when different amounts of acid are added to the latex, coagulation takes place with small and with large doses, but between these is a „gap” in which the latex remains milky. Sufficient quantities of salts, however, decrease this gap or eliminate it wholly, and for some acids (amongst them sulphuric acid according to some authors) coagulation is produced with all amounts and no „gap” occurs, which fact has been explained by saying that ordinary latex contains enough salts to make the gap disappear. Though experimental results have been secured from several sources, they are still far from sufficient to clear up these rather complicated phenomena, especially as only diluted latices have been experimented with by most investigators.

Attention was first drawn to the differences between certain acids in this respect by J. PARKIN (Circ. R.B.G. 1 (1899), 148) who found the range, over which good coagulation occurs for acetic acid, much greater than for other acids, and regarded this as a distinct advantage in estate-practice.

W. CROSSLEY (I.R.J. 41 (1911), 1206) found the maximum amount of acetic acid to be 20 times the minimum, calculated on the acid added, or 10 times, when the acidity of the latex (which

was preserved with formalin, and contained only 7 % rubber) was taken into account. This minimum amount however was taken rather high, being 1 acetic acid added in 82 parts of rubber, or 0.85 gm. per liter 7 % latex. The maximum amount allowable was found to increase on dilution of the latex, so that in dilute latex the „safe region” is larger. In an experiment with dialysed latex (I.R.J. 42 (1911), 1342) the maximum for acetic acid was found to be 9 times the minimum, for formic acid 2.7, for hydrochloric acid 4.0 times, and for sulphuric acid 3.6 times the minimum.

These figures have however been criticised by B. J. EATON (Bull. F. M. S. No. 17 (1912), 10), who worked with fresh, undiluted or dilute latex in the East. EATON found the degree of dilution to be of great importance, and remarked further that coagulation, when not obtained immediately, often followed after some standing, being caused by the acid first included in the clot. He obtained coagulation with every quantity of acid (even of hydrochloric acid), when using undiluted latex, and acid in such strength that the final mixture was sufficiently concentrated.

G. S. WHITBY (VIII Int. Congr. 25, 612; also I. R. J. 45 (1913), 945; also Z. Koll. 12 (1913), 156; further Agric. Bull. F. M. S. 6 (1918), 381) studied these phenomena, using 10 % to 12 % latex, for acetic and some mineral acids; he found the gap, in which no coagulation occurs, very distinct for hydrochloric and nitric acid, and only indistinct for sulphuric acid, whilst large amounts of acetic acid produce no coagulation, so that in this last case the gap shows no limit on the side of large amounts of acid.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 37; also Z. Koll. 13 (1913), 219), also working with a dialysed preserved latex with 17 % total solids, found no gap for sulphuric acid, so that this acid can be used over a greater range than acetic.

N.W. BARRITT (J.S.Ch.I. 33 (1914), 289; also I.R.J. 47 (1914), 751) studied the effect of salts on this „gap”, and found the range, within which no coagulation occurs, to decrease with increasing quantities of salts. The latex in his experiments was added in an amount of 1 part to 100 parts of solution of acid and salt. From the fact that EATON (see above) found no „gap” for coagulation of undiluted latex with sulphuric acid, BARRITT concludes that the concentration of salts in latex corresponds to at least $\frac{1}{25}$ normal sodium sulphate (= 2.8 gm anhydrous salt per liter).

The argument, that for some acids the range in which complete coagulation is obtained is much greater than for

others, has now wholly lost its practical importance, as the acid, for evident economic reasons, is always applied in so nearly the minimum amount that the maximum is never approached; the existence of a maximum is even completely unknown to most practical men. For the study of the phenomena of coagulation, however, this point is of much interest.

The oldest explanation, given by J. PARKIN (Circ. R. B. G. 1 (1899), 149), was that small amounts of acid neutralise the alkalinity of the latex, and precipitate the protein, whilst larger amounts of acid again dissolve the protein. This is evidently false, as the alkalinity of latex, if indeed it exists, is very small (see § 9), and because ordinary, naturally acid latex shows the same phenomena when increasing amounts of acid are added.

Some relation with the precipitation and redissolving of protein has been assumed by several investigators (see, for instance, G. VERNET, Bull. Mars. 1 (1919), 107; Bull. Saigon 1 (1919), 344).

G. S. WHITBY (Agric. Bull. F. M. S. 6 (1918), 381) holds the action of relatively small amounts of acid to be due to the intermediation of enzymes, but supposes large amounts of acid to work as direct protein-precipitants.

The absorption-phenomena that accompany coagulation by acids, and the amount of acid in the serum and in the clot, have not yet sufficiently been investigated.

W. CROSSLEY (I. R. J. 41 (1911), 1206) showed that very nearly the total of the added acetic acid plus the natural acid in latex is found by titrating serum plus coagulum with caustic soda, from which he concludes that the acid is not bound chemically, but only physically. A large part of the acid however is absorbed by the coagulum, and is not easily washed or dialysed away (I. R. J. 42 (1911), 1293 and 1341). This amount increases as an exponential function of the amount of acid added.

Influence of dilution.

Dilution retards coagulation; for practical purposes, to obtain a clot of the desired hardness in the desired time, less acid has to be added to concentrated latex than to diluted.

Sometimes the opinion is heard that only the ratio of acid to rubber is decisive for coagulation, so that in con-

centrated and diluted latex the same amount of acid, calculated on the rubber, would have to be added. In how far this holds for the arresting of the Brownian movement or for the first stage of flocking or precipitation, remains to be seen; but in practice, for obtaining coagulation in an economic way, that is, slowly and with as little acid as possible, the dilution is undoubtedly a point of importance.

A constant ratio between acid and rubber, independent of degree of dilution, was assumed by J. PARKIN (*Circ. R. B. G.* 1 (1899), 148; and *Ann. Bot.* 14 (1900), 196; see further *I. R. J.* 45 (1913), 1193 and 1298). The constant ratio between total acid (acidity of latex plus acetic acid added) and rubber was found by W. CROSSLEY (*I. R. J.* 41 (1911), 1206) to hold good for a diluted latex of 7% and greater dilutions, and for clotting within half an hour.

This could not be confirmed for a dialysed latex (free from acid) investigated by Cl. BEADLE and H. P. STEVENS (*VIII Int. Congr.* 9, 34; also *Z. Koll.* 13 (1913), 217), who found increasing milkiness of the serum when diluting the latex and adding the same amount of acid per unit of rubber.

The question was further investigated by B. J. EATON (*Bull. F. M. S.* No. 17 (1912), 9) and S. MORGAN (*Prep. Pl. Rubber* page 216), who proved that Parkin's assertion does not hold good. For further discussion by J. PARKIN see *I. R. J.* 45 (1913), 1193, where the conditions under which his experiments were made are explained.

The quantitative relations between acid, dilution, and formation of clot within a certain time are not yet sufficiently established; it is not easy to follow such a process as coagulation quantitatively, as once in course of progress it is furthered by moving or stirring, and even when the coagulating mass is strained rapidly, the still fluid latex enclosed by the spongy clots or flakes may partly coagulate before it can be removed. Some data for coagulation with acetic acid from actual practice may however be added to give a general idea.

Adding 1 part of strong acetic acid to 100 parts of rubber will give a rapid coagulation when the mixture is undiluted, and contains for instance some 30% of rubber: a hard coagulum may be formed in half an hour. When the mixture (latex) however is diluted, say to 15%, some 1 1/2 hours

will be necessary. When 1 part acid to 150 parts rubber is used, these figures change to appr. 1 and 6 hours respectively; and a ratio of 1 part acid to 200 parts rubber will give a workable coagulum only after two hours, when the latex is undiluted, and after 12 hours in a dilute latex.

§ 75. Influence of the non-rubber constituents of latex.

Though for practical purposes the role of the non-rubber constituents of latex needs no special attention (these substances being always present), for the study and explanation of coagulation they may not be left out of account. As a matter of fact, the removal of these substances completely changes the phenomena of coagulation. Many substances lose their coagulating effect on dialysed latex, amongst them alcohol and the salts of monovalent metals. The salts of bivalent metals, and many acids, produce only creaming or flocking, and no coagulation, whilst trichloroacetic acid and acetone are coagulants for dialysed latex.

V. HENRI, C.Gp. 1906, 512, see also § 90 and 99.

From his studies on the combined influence of salts and acids, N.W. BARRITT (J S.Ch. I. 33 (1914), 289; also I.R.J. 47 (1914), 753) concluded that the non-rubber constituents of latex have at least as much influence as a 1/25 normal solution of sodium sulphate.

P. DEKKER (Comm. Delft I, 27) also stated that the dissolved compounds in latex play a role, as coagulation in dialysed latex was incomplete, but when a drop of dialysate was added coagulation became easier.

On the other hand Cl. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 24 and 32; also Z. Koll. 13 (1913), 211 and 216) found latex (which had been preserved with ammonia) to react normally after dialysation, so that the crystalloids did not seem to play any part in the coagulation.

Many of the discrepancies found in present literature are solely to be ascribed to the fact that the latex experimented with was either diluted or dialysed; in both cases the influence of the serum-substances on coagulation is greatly altered, and this may change the whole aspect of the question.

§ 76. Theory of the electrical charge.

The particles of emulsions and suspensions show an electrical charge; the rubber globules in latex have a negative charge, and when an electric current is passed through latex (or at least through dialysed preserved latex) the globules move with the current and accumulate at the anode, whilst in the neighbourhood of the cathode the latex clears up.

V. HENRI (C. R. 144 (1907), 432; C. Gp. 1906, 513) made this statement for latex preserved with ammonia and dialysed free from soluble substances.

The electrical current as a method of separation was applied on a practical scale by P. S. CLIGNETT (Rubb. Rec. 1914, 374), compare § 194.

It has, however, not yet been proved that this coagulating action of the electrical current consists in a simple kataphoresis, and that electrolysis of serum-substances (salts) does not play a role. In fact, no satisfactory experimental data are available on the action of an electric current on fresh, undiluted and undialysed latex.

Just as is the case with other suspensions, latex is flocculated by electrolytes, the active part being the positive ion. Acids act strongly in this way, whilst salts of polyvalent ions have a much greater effect than those of univalent metal-ions. The exact electrical conditions of latex have however not yet been established and it is, for instance, not yet known whether the flocking takes place at or near the iso-electrical point.

These phenomena were especially put in the foreground by V. HENRI (C. R. 144 (1907), 432; C. Gp. 1906, 513), who distinctly stated that coagulation of latex by electrolytes is determined by their positive ions, so that acids are coagulants and alkalies are not, bivalent ions have a stronger action than monovalent etc. HENRI however based his conclusions only on investigations on dialysed latex, so that the influence of the soluble substances in natural latex is left out of account. PH. SCHIDROWITZ (Rubb. Rec. 1914, 304) discussed the different methods of coagulation from the point of view of electrical conditions, and pointed out that the latter may be influenced, besides by electrolytes, by all such factors as heat,

dilution, mechanical action, action of various rays, addition of colloids, and addition of substances that affect surface-tension or have a solvent or precipitant action on one or more of the constituents of the suspension (such as benzol or alcohol). Of course the change in electrical conditions may be accompanied by other (for instance chemical) changes also.

Coagulation in alkaline media (such as by calcium chloride and other salts in ammoniacal solution) can be explained in the same way, in analogy with other suspensions, the charge of which is changed when the reaction of the liquid changes.

Whilst the simple ionic action of electrolytes may be sufficient to explain their action as coagulants in many cases, certainly far from everything about coagulation is said by simply stating the loss of, or change in electric charge.

Coagulation by heat or freezing, though they may be accompanied by a change in electrical conditions, need a further explanation, and the action of such agents as alcohol, acetone and other non-electrolytes also is accompanied by other phenomena.

Supporters of the protein-theory draw attention to the fact that the electrical phenomena certainly may play a role in coagulation, but that it may be especially the proteins in the rubber-globules that are thus affected (see § 77).

§ 77. The role of proteins.

In its oldest form the protein-theory of coagulation supposed the rubber globules to be surrounded by a thin film of protein, which stabilised them and protected them against outer influences. When by some influence — heat, chemicals and so on — the protein was attacked and the film broken, the rubber globules would be able to clot together and precipitate. In accordance with more recent views in colloid chemistry the proteins are now no longer supposed to form a distinct film around the rubber globules, but to exercise a protective action, the mechanism of which is not further described, but which is compared with the well-known action of other protective colloids.

According to this modern protein-theory, the action of

all known coagulants may be explained as an action on the proteins, which are supposed to be the medium that is actually coagulated, the rubber globules following when the protective colloid is taken away.

R. H. BIFFEN (Ann. Bot. 12 (1898), 170) supposed the proteins to be the substances most likely to be attacked by acids, salts, heating etc. This idea was further worked out by J. PARKIN (Circ. R. B. G. 1 (1899), 146).

C. O. WEBER (Ber. 36 (1903), 3108), on the basis of his studies on *Castilloa*-latex, supposed coagulation in all latices to be caused by a precipitation of the proteins, which he assumed to form a film around the caoutchouc-globules. He distinguished (Trop. Agric 23 (1904), 653) coalescence (for instance by adding formalin and then sodium sulphate, see § 90) in which a rubber free from protein is said to separate in a thick creamy mass, from coagulation proper, caused by reagents which precipitate the albumens. His conclusions have however been criticised by A. W. K. DE JONG and W. R. TROMP DE HAAS (Ber. 37 (1904), 3301).

E. FICKENDEY (Z. Koll. 8 (1911), 44) rejected the idea of a protein film, but regarded the protein as a protective colloid.

F. FRANK (Kunststoffe 1912; see G. Ztg. 27 (1912), 1718 and Z. Koll. 16 (1915), 11) put stress on the fact that all reagents that precipitate proteins also cause a separation of the caoutchouc from latex; he compared the action of a number of substances on the proteins in different latices with their coagulating effect.

The protein-theory was again put in the foreground by G. VERNET (Bull. Mars. 1 (1919), 107, see further Bull. Saigon I (1919), 342 and C.Gp. 1920, 10193), who points out that the following methods of coagulation present a close resemblance to the coagulation of proteins:

coagulation by acids, by certain alkalies, by salts, heat, alcohol, formaldehyde, in accordance with dose and temperature, acetone, tannin, smoke, essential oils, chloral.

further such substances as carbondisulphide, carbon tetrachloride, ether, benzene, chloroform, which, though they are caoutchouc-solvents, precipitate the rubber from latex.

The coagulation of boiled diluted latex (to exclude enzymes and bacteria) by strong acetic or mineral acids, the re-solution of the still flocky precipitate in an excess of acid, and the renewed precipitation by adding either a base (ammonia), or another portion of boiled diluted latex to this solution, strongly resemble the reactions shown by proteins.

In the same way the „gap” in coagulation with mineral acids (that is the fact that small quantities and large quanti-

ties produce coagulation, but intermediate quantities do not, see § 74 and 89) and the influence of salts on the coagulation with acids (see § 75 and 90) are very similar to what is observed in the precipitation of proteins.

VERNET tried to furnish further proof by extracting water-soluble proteins from thin films of latex rapidly dried in the air, and studying their reactions. Investigations on this point, if followed up further, might well lead to valuable conclusions.

Whilst, as a matter of fact, many and perhaps all methods of coagulation may be reconciled with the view that the proteins are first attacked, this analogy should not be taken as a direct proof, which in most instances is still lacking. Direct investigations on the part played by proteins are still scarce and not conclusive; and besides proving the fact that the coagulants really act on the protein, it should also be demonstrated that the *course* of coagulation in each case, not only qualitatively but also quantitatively, and its velocity and progress, are strictly the same as when these coagulants (with the same by-products) act on the proteins of latex.

Further investigations on latex treated with enzymes such as papain and trypsin, by which the proteins are decomposed so that they may be removed by dialysis, would be of much importance in clearing up this point.

D. SPENCE (Lectures 1908, 195) found that more than half of the protein in latex can be removed by digesting with trypsin without coagulation taking place, so that the stability of latex is not dependent upon an unchanged protein-content.

From the investigations of H. C. T. GARDNER (Rubber. Ind. 1911, 227) and A. J. ULTÉE (Teysm. 28 (1917), 175) it is clear that latex digested with papain still coagulates and gives a coherent clot, from which it would follow that neither coagulation, nor coherence of the clot are dependent upon the presence of proteins. It was however not proved that all protein had been removed or decomposed in these researches, so that they are not wholly conclusive. See also § 104.

A further issue, which deserves attention, is the fact described by G. VERNET, (Bull. Mars. 1 (1919), 111) that latex, to which $\frac{2}{3}$ of its volume of milk is added, may be coagulated by the addition of rennet, so that in that case the precipitation of the casein apparently causes the coagulation of the rubber globules, much in the same way as the flocculation of the latex-proteins is supposed to do in normal coagulation.

In discussions of this point it has sometimes been forgotten that, taking coagulation to be in most or all cases in the first instance a reaction on the proteins, excludes neither the electrical theory, nor that of the role of enzymes. In fact, proteins show to a high degree the phenomena of flocculation and re-solution due to changes in the electrical charge, and it would seem very logical to suppose that the proteins with their amphoteric chemical character in the first place absorb electrolytes and give a charge to the suspension, and that it is not the inert caoutchouc-hydrocarbon which does this.

Further, a reaction between coagulant and protein may very well be catalysed in certain circumstances by an enzyme; or the protein acted upon may even be identical with the enzyme.

Investigations on these questions have in many respects been too cursory to allow of any definite conclusion; but the view that the proteins play a role in coagulation can certainly not be put aside and deserves further elaborate study.

§ 78. The role of enzymes.

Some authors suppose that an enzyme, called coagulase, present in latex as it exudes from the tree, plays an active role in coagulation, at least in a number of cases.

The action of enzymes in spontaneous coagulation was first drawn attention to by D. SPENCE (Lectures 1908, 198), further worked out by G. S. WHITBY (VIII Int. Congr. 25, 604; also I. R. J. 45 (1913), 941 and Z. Koll. 12 (1912), 151) and subsequently supported by L. E. CAMPBELL (J. S. Ch. I. 36 (1917), 274), and M. BARROWCLIFF (J. S. Ch. I. 37 (1918), 48 T). V. CAYLA (I. R. J. 39 (1910), 563) mentions a coagulating enzyme in fresh latex of *Ficus elastica* and studied its coagulating effect on sterilised cow's milk.

Now, enzymes are organic catalysers of complicated and mostly unknown composition, which accelerate or make possible the reaction between certain substances; they are destroyed by heat, mostly at 80°, and are sensible to small additions of other substances, which may activate or paralyze

their catalytic action. To prove that an enzyme plays a role in coagulation therefore means to prove that coagulation cannot proceed as it does without the intervention of this catalyst, and does not proceed when the enzyme is paralyzed. The study of a latex free from enzyme, which would furnish the most direct proof, is out of the question, as the enzyme is supposed to originate either in the latex-vessels themselves, or from the adjoining vessels cut open by tapping, so that enzyme-free latex is not obtainable.

A coagulating enzyme has not yet been isolated from latex either in the pure form, or in an impure but somewhat concentrated form.

Many arguments have been brought forward in favour of the presence of an enzyme; but some of them are based only on analogy, which is no proof, and others can also be explained without enzyme action. The experimental material at hand does not yet seem sufficient to allow of a decision, and the whole question will have to be investigated more thoroughly and systematically.

The remark may not be out of place that the hypothesis of enzyme activity during coagulation does not do away with the other above named theories; the enzyme, as a catalyst, only changes the speed or course of the reaction, without altering the reagents or the product. Also, when an enzyme plays a role in coagulation under certain circumstances, this does not mean that it is at work in every method of coagulation, but only that it influences the speed or course of coagulation in that special case. That coagulation without enzyme action is possible, is for instance evident from the fact that it may be effected by heat, at temperatures which destroy the enzymes.

Some of the principal arguments for an enzyme action are:

- 1) Diluted latex may be boiled without coagulation taking place; this boiled latex does not coagulate on addition of small quantities of acetic acid in the same way as unboiled latex does, but addition of a few drops of fresh latex restores the normal coagulation.

M. BARROWCLIFF J. S. Ch. I. 37 (1918), 49 T; G. S. WHITBY, Agric. Bull. F. M. S. 6 (1918), 374. See further Cl. BEADLE

and H. P. STEVENS (VIII Int. Congr. 9, 33; also Z. Koll. 13 (1913), 216).

G. VERNET, (Bull. Mars. 1 (1919), 115; further Bull. Saigon 1 (1919), 344) mentions that boiled diluted latex coagulates on addition of acetic acid, but does not state the quantity of acid added nor give such details as show that the effect of the acid and the course and velocity of coagulation are the same as in unboiled latex.

This may be explained as the action of a catalyst, which is destroyed by heating; but modification of the proteins by heating the diluted latex may also play a role, and the inoculation with fresh latex also brings in bacteria, so that this argument, to be conclusive, would have to be carried further.

2) The course and velocity of coagulation of latex by acetic acid resemble more the coagulation of milk by the enzyme rennin than the ordinary acid coagulation of rennin-free milk. In the last case coagulation is immediate and rapid, once a certain critical degree of acidity is reached; acid in smaller amounts has an anti-coagulating effect, as it hinders the action of the lactic acid bacteria. On the other hand latex, like milk to which rennin is added, coagulates even with small quantities of acid; the speed of coagulation (the time in which a clot is formed) depends upon the amount of acid added and the dilution of the mixture, but coagulation in the end is obtained with small as well as with large amounts of acid.

Small amounts of acid added to latex do also inhibit the growth of micro-organisms, so that less putrefaction or gas-formation takes place; but they have no anti-coagulating effect, the coagulation only goes on more slowly.

M. BARROWCLIFF, l. c; see especially G. S. WHITBY, Agric. Bull. F. M. S. 6 (1918), 374.

The course of latex-coagulation with small amounts of acid and the time-factor in these cases are indeed far from explained. To make the hypothesis of the action of enzymes, activated by small amounts of acids, conclusive, it would be necessary to know how dilute acid acts on the proteins

in latex (which reaction need not be spontaneous, but may perhaps proceed slowly); and what role is played by the natural acidity of latex, or how sterile latex behaves on the addition of small amounts of acid.

3) Certain coagulants, such as alcohol and tannic acid, produce a different type of coagulation, which is immediate; they may give not a coherent, but a floccular precipitate. These substances are supposed to act directly (perhaps as protein-precipitants), without the intermediation of an enzyme. The same is supposed to be the case with large amounts of mineral acids, which produce immediate coagulation (see § 74 and 89.).

4) The natural coagulation of latex is not inhibited or retarded by bactericides like toluol or thymol, which are harmless to enzymes; but agents such as hydrocyanic acid and potassium cyanide, which are bactericides and at the same time paralyze enzymes, inhibit it.

M. BARROWCLIFF, J. S. Ch. I. 37 (1918), 49 T; G. S. WHITBY, Agric. Bull. F. M. S. 6 (1918), 380. The actual proof that no bacteria develop and that no natural acidity is produced, when toluol or thymol is added, however is still wanting, and the point therefore will have to be further investigated.

M. VERNET (Bull. Saigon I (1919), 346; also C. Gp. 1920, 10195) draws attention to the coagulating effect of thymol in larger doses.

The activating action of calcium salts and the inhibiting action of formalin, which have also been brought forward in support of the enzyme theory, are arguments too feeble to be given any importance. Calcium salts are strong coagulants (see § 76 and 90), whilst all salts influence the course of coagulation or flocculation in all cases, even when no enzyme is present. Formalin inhibits bacterial action, and may act only in this way; further a latex, to which formalin is added, coagulates perfectly well with acetic or other acids, calcium chloride and so on, so that in such a case the action of formalin, i. e. its paralysing effect on enzymes, cannot prevent coagulation.

From this discussion it will be seen that, though the action of enzymes in coagulation is not proved, it deserves attention and may perhaps on further research be found to clear up certain details of the course and velocity of the process.

§ 79. Spontaneous coagulation.

A special interest has been shown in the explanation of spontaneous coagulation, especially as regards the role of enzymes or bacteria.

As is discussed in § 13 and 94, latex after it exudes from the tree rapidly becomes contaminated with bacteria, which develop acids in appreciable amount. There is little "doubt that these acids play a role in spontaneous coagulation, because the coagulation may be retarded or prohibited by neutralising the acids by bases, or by sterilising the latex and preventing the growth of micro-organisms. The further point, however, as to how these acids produce coagulation: by activating the enzymes, by precipitating the proteins, or in some other way, is not yet settled to general satisfaction. There are several interesting facts about these phenomena, which are still unexplained. For instance the amount of acid formed spontaneously in latex, before coagulation begins, is much greater than the dose of acetic acid necessary to obtain coagulation.

The action of bacteria in spontaneous coagulation was already assumed, though not proved, by J. PARKIN (Circ. R. B. G. 1 (1899), 145).

G. VERNET (Bull. I. Ch. 14 (1911), 825; also C. Gp. 1912, 5862; further Bull. Mars. 1 (1919), 113), who first propounded the bacterial theory, and with A. DENIER (C. R. 165 (1917), 123) isolated the micro-organisms causing acidity (see § 96), admits that these micro-organisms may act through the medium of a diastase or acidase, which they secrete, but regards the supposition of the action of an enzyme present in latex as superfluous.

The action of micro-organisms was then independently defended again by B. J. EATON (Agric. Bull. F.M.S. 4 (1915), 26, and *ibid.* 6 (1917), 156, see further Bull. F.M.S. No. 27 (1918), 276), whose experiments were criticised by

M. BARROWCLIFF (J.S.Ch I. 37 (1918), 49 T) and G.S. WHITBY (Agric. Bull. F.M.S. 6 (1918), 381).

K. GORTER and N. L. SWART (see Agric. Bull. F.M.S. 5 (1916), 48 and § 94—96) further studied the formation of acids by micro-organisms and the phenomena accompanying spontaneous coagulation.

An important issue for obtaining clearness on this point is, of course, the behaviour of sterile latex, that is latex collected in such a manner as to protect it against all contamination with bacteria. It seems that such latex does not show coagulation, even after several days or a month's keeping, so that the fact that the formation of acids by micro-organisms plays a role in spontaneous coagulation, may be regarded as settled.

G. VERNET (Bull. Mars 1 (1919), 115) mentions experiments by KREMPF and H. SCHEIN on sterile latex, which point in this direction, though the latex was not obtained in a completely sterile state.

Similar results were communicated by W. H. ARISZ in a planters lecture (1919).

§ 80. Other views about coagulation.

Several other explanations or theories on coagulation have been offered, but it is dubious whether they have any importance for Hevea-latex. Investigators, studying latices of a totally different composition, have often not sufficiently restricted their conclusions, so that the reader may be inclined to apply their views to Hevea-latex also, though, perhaps, this was not the intention of the author, and is certainly not feasible. Latices, for instance, in which certain resinous substances play the role of protective colloids, or in which the rubber globules are much larger than in Hevea, show totally different coagulation-phenomena, which are to be explained in a different manner. To show how different the behaviour of various latices may be, we need only mention the fact that latices such as *Castilloa* and *Funtumia* easily cream on addition of water; and that formaldehyde, which is a preservative for Hevea-latex, acts as a strong coagulant on *Funtumia*-latex.

Proteins have been made responsible for the coagulation of latices other than Hevea also. We have already mentioned the conjecture of C. O. WEBER for Castilloa-latex (see § 77). Coagulation, in parallel with the flocking out of proteins, was studied in latex of Funtumia and Landolphia by G. FLAMANT (C. Gp. 1912, 5940), who found the role of different proteins very important in these latices.

Peptones are regarded as the active part in the coagulation of Funtumia-latex by E. FICKENDEY (Z. Koll. 8 (1911), 45) and F. FRANK (Kunststoffe 1912, see Z. Koll. 16 (1915), 12), because in this latex dialysis and an addition of formalin cause coagulation.

Resins are supposed to play the active part in the coagulation of Landolphia by HEIM and MARQUIS (Ann. Pl. Ind. Ch. 1915, 103).

A simple carrying (in a purely mechanical way) by a foreign and chemically inactive precipitate, which is formed in or added to the latex, is supposed by HEIM and HENRIET (C. Gp. 1913, 7422) to be able to cause coagulation in Funtumia or Landolphia-latex.

CHAPTER VI.

METHODS OF COAGULATION.

The number of coagulants and of methods of coagulation is legion. Over a period of more than twenty years scientists and planters have been busy with coagulating media; hundreds of substances have been tried for their coagulating efficacy and for many of these the effect on the rubber and the economic side of the question have been established by elaborate research. The result is that the great majority of estates — in Java about 99 % — use acetic acid as a coagulant. Still there appear from time to time inventors who claim to have found a new and better coagulant. After all that has been done and written along this line, it is evident that there is but a small chance that a change will take place, unless economic conditions or the requirements of the market wholly change. Because these inventors, however, still find those who believe in them and who are attracted by their pretensions as insects are to a lamp, it may be well to preceed the discussion of a number coagulants by a short review of the requirements which a good coagulant must fulfill.

§ 81. What is required of a good coagulant?

1. It must produce a good coherent workable coagulum, from which a rubber of a good external appearance can be obtained.
2. It must, under all circumstances which occur on estates, give a good coagulation with either dilute or undiluted latex of varying composition etc.
3. The limits within which a good coagulation is obtained must not be too narrow, so that in practice no danger is run of rendering the coagulation incomplete either by using a little too little, or a little too much of the coagulant.

4. It must not be detrimental to the quality of the rubber.
5. Applied according to the methods of working as they are carried out on estates, and by assistants often with little training, it must produce a rubber which is at least as uniform as that produced by the means now in use.

On this point the pretensions of the inventors are generally very great. "Uniform" and "Standard rubber" are always the first claims that one hears for a new medium, but every trace of evidence is commonly lacking that this is anything more than a claim. It should not be forgotten what extensive research, under varying conditions, and on different estates, is necessary to fully determine whether a new process is really better than those now in use.

6. It must be easy to use even by an untrained personell and must not be dangerous to handle.
7. It must be obtainable in large quantities of practically the same composition.
8. It must be at least as cheap as the media now used.
9. The total of these properties must give a noticeable advantage over acetic acid, so that an alteration in methods is profitable enough to overcome the difficulties of arranging a method of work and perhaps of putting a new product on the market.

§ 82. Principal methods of coagulation.

Before discussing in detail the properties of different coagulants, we will here briefly review the practical phase of the question.

The bulk of plantation-rubber is prepared nowadays by the aid of *acetic acid* (§ 83).

Its nearest relative, *formic acid*, has never made great advances (§ 87).

Sulphuric acid in the beginning of the war was used on a rather large number of estates in some countries, but its use is now nearly completely abandoned (§ 86).

Alum has been used on European estates in exceptional cases, and is still largely used by native planters. The disadvantages of its use are well known, and measures have been taken or considered to drive it out completely (§ 88).

To replace acetic acid, a coagulant such as *fermented coconut milk* would seem a much better medium than alum for native planters; on large estates such fluids have sometimes been used, but are now replaced by acetic acid.

Spontaneous coagulation in the absence of air, now tried only on an experimental scale, deserves attention, though its advantages are not so great as they are sometimes supposed to be (see § 95 — 97).

Preparation according to the *Brazilian method*, as yet still in the experimental stage on a large scale, deserves attention (see Chapter XIV).

Preparation of *matured rubber*, either in the form of slab, crepe or block, though in use on some estates working under special conditions, is still in the experimental stage for estates working for the open market (see § 192).

§ 83. Acetic acid.

Acetic acid, which is in common use as a coagulant, of course satisfies the requirements mentioned in § 81 to a high degree.

Smoked sheet or first quality crepe, not coagulated with acetic acid, is today a great exception; and though suggestions and trials with other coagulants are not absent, decidedly more than 95 % of all first quality plantation-rubber may nowadays be assumed to be prepared with acetic acid.

One of the first to draw attention to acetic acid was R. H. BIFFEN (Ann. Bot. 12 (1898), 166) who found it in the smoke used in the Brazilian method of preparation. Its use was then further studied by J. PARKIN (Circ. R. B. G. 1 (1899), 144; Ann. Bot. 14 (1900) 196; I. R. J. 40 (1910), 752 and 46 (1913), 919; see further the review in I. R. J. 45 (1913), 1193), and by many others.

Proportions used.

In practice the proportion between the acid used and the rubber obtained fluctuates from about 1 : 80 to 1 : 280, and one may assume that in the majority of cases it remains within the normal limits of 1 : 150 to 1 : 200, or 0.75 gm.

to 1 gm. of acetic acid per liter of 15 % latex. More than double the normal, or less than $\frac{2}{3}$ of the normal quantity seldom or never occurs in actual practice.

The statements as to the amount of acid necessary for coagulation were very divergent in former days, and much larger amounts have been prescribed by several authors; see for instance W. CROSSLEY (I. R. J. 41 (1911), 1205); J. PARKIN, l.c.

The older figures perhaps relate to instantaneous coagulation and probably often to very dilute latices; in estate-practice immediate clotting is not desirable, and coagulation in two hours is regarded as rapid. Often, to spare acid, the latex is left to coagulate overnight.

Later figures have been given by B. J. EATON, (Bull. F. M. S. No. 17 (1912), 8 and 16); CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 33; also Z. Koll. 13 (1913), 216); S. MORGAN (Prep. Pl. Rubber, page 215), whilst J. PARKIN discusses the older and newer results in I. R. J. 45 (1913), 1193.

The above mentioned figures have been sufficiently established by long practice on estates and are now generally adhered to.

From the following it will be seen that the deviations in the quantity of acetic acid, within the usual limits, are no cause of variability in the product. From this it follows that the quantity of acetic acid can be regulated according to practical demands such as economy in its use, and the obtaining of a coagulum of the desired hardness in the desired time. Another use, for keeping the rubber pale by taking larger quantities of acetic acid, has wholly lost its significance since the introduction of bisulphite has become common (see § 12, 48 and 51).

In fixing the amount of acid, one has to take into account that the process of coagulation depends upon the proportion of all three components (rubber, strong 'acetic' acid and diluted serum) in the mixture which has been set to coagulate, as we saw in § 74. In proportion as the mixture is more or less concentrated, either in rubber or acetic acid, so the coagulation proceeds more or less rapidly; in proportion as there is more acid in relation to the rubber, the coagulation is more rapid, and in so far as the rubber content of the mixture is higher, the coagulum is harder. It has been supposed by some that the proportion of acetic acid to

rubber only is decisive in coagulation, but this is just as incorrect as the still wide spread notion, that one must add a certain quantity of acetic acid per liter of latex, regardless of whether it is diluted or undiluted (see § 74). Some examples, showing how the velocity of coagulation is influenced by the amount of acetic acid added, have already been given in § 74.

Concerning the requirements as to the clearness of the serum for a complete coagulation, we will speak in § 115.

It may further be mentioned that, in using such chemicals as formalin, sodium sulphite and bisulphite, the quantity of acetic acid must be increased (sometimes by $\frac{1}{3}$ or $\frac{1}{4}$). This, however, as we will see on page 168, gives no perceptible differences in the properties of the rubber.

Further it has to be taken into account that the condition of the latex may be of some influence. It is, for instance, often observed that in the time of wintering, and especially when the new leaves are developing, the quantity of acetic acid has to be increased somewhat to obtain the ordinary, satisfactory coagulation. In how far this is connected with a decrease in sugar-content (see § 8 and 21) or of other constituents of the latex, or by a decrease in natural acidity has not yet been determined.

The exact relation between natural acidity of the latex and quantity of acid to be added for coagulation has not yet been worked out.

Dilution of the acid.

It may be well to draw attention to the fact that the dilution, in which the acetic acid is added, is without significance for the properties of the coagulum and for the inner properties of the rubber. The dilution of the acetic acid only serves to make the mixing of latex and acetic acid easier, and to prevent too quick coagulation by a local excess of acid in the places where the acid is poured into the latex. For the completeness and the velocity of coagulation, given a latex with a certain rubber content, the quantity of strong acetic acid, which is administered, is alone decisive, without

regard to whether one adds it in a concentrated or in a dilute solution.

Regulation of the coagulation by adding a fixed quantity of an acid which is diluted more or less according to needs, is irrational. It is better to change the total quantity of diluted acid, but to retain the dilution of the acid once chosen. When for instance coagulation is imperfect after using 30 cc of $2\frac{1}{2}\%$ acetic acid, the practice sometimes is to use still 30 cc, but of a stronger acid, for instance 3% ; but the use of 36 cc $2\frac{1}{2}\%$ acid has the same effect, and is easier, as the same stock-solution can be used. In other words, it is not the strength of the diluted acid, added to the latex, that determines coagulation, but only the strength of the final mixture of latex, water and acid set to coagulate, or the degree of dilution of the acid in this final mixture. Only in the case of an already very dilute latex being further diluted by the use of a weak acid, is the use of strong solutions of acid an advantage.

In the preparation of sheet-rubber a 1% acid is generally chosen, but higher concentrations (for instance $2\frac{1}{2}\%$) are also satisfactory; in crepe-preparation concentrations up to 5% can be used.

The water used in diluting the acid influences the process of coagulation only in so far as it increases the total quantity of water in the final mixture. In coagulating 1 liter of 15% latex with 80 cc of 1% acetic acid, one actually sets a liquid with a rubber content of 13.9% to coagulate. From the table in § 64, however, it is evident that this does not produce any marked differences in the inner properties of the rubber.

Influence on the properties of the rubber.

Within the limits mentioned above the influence of variation in the amount of acetic acid on the properties of the rubber is small. The tensile strength and slope present no change, while the time of cure and viscosity decrease somewhat with increasing amounts of acid.

For amounts of acetic acid larger than the normal, the differences in crepe-rubber are about as follows.

	Decrease in time of cure	Decrease in viscosity
Double the quantity . . .	0 — 5 min	0 — 4
Quadruple the quantity . .	5 — 10 „	2 — 7

See O. DE VRIES (Arch. I (1917), 36 and 40).

H. P. STEVENS (Bull. R.G.A. 1 (1919), 39) gives the following increases in time of cure (in percent of the time of cure for the minimum quantity of acetic acid, which is taken as 1 part acid to 1200 parts latex):

	Crepe	Smoked sheet
4 times minimum quantity . .	15 %	11 %
8 „ „ „ . .	25 „	22 „
16 „ „ „ . .	34 „	33 „

Ph. SCHIDROWITZ and H. A. GOLDSBROUGH (I.R.J. 44 (1912), 1149) found the rate of cure to decrease with increasing amounts of acetic acid (varying over a range of from 1 to 24 parts) with differences of approximately the same order as the above. The viscosity (for which however no figures are given) was highest for the sample prepared with the smallest dose of acid.

B. J. EATON and J. GRANTHAM (Agric. Bull. F. M. S. 3 (1915), 223; Bull. F. M. S. 27 (1918), 203) found in the preparation of crepe an increase in rate of cure of 10% with 5 times the minimum amount of acetic acid.

In experiments by L. E. CAMPBELL in Ceylon (Bull. Ceyl. 23 (1915); Bull. Imp. Inst. 14 (1916), 502; *ibid.* 16 (1918), 412) no appreciable increase in rate of cure in unsmoked sheet was found with a double amount of acetic acid, whilst the tensile strength remained the same.

CL. BEADLE and H. P. STEVENS (Rub. Rec. 1914, 360) mention that excess of acetic acid causes the different forms of set (deformation) after a fixed cure to increase, that is it causes the rubber to cure slower.

Since the double quantity is seldom used in practice, and the fourfold quantity probably never, the decrease in rate of cure and viscosity caused by varying doses of acetic acid is not the cause of marked variability in the product.

Also, when the rubber was kept for a long time, no deterioration in inner properties could be detected, when large doses, such as those described above, were used.

See also PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 44 (1912), 1198).

The largest amount of acetic acid used in practice occurs in trial coagulation; a ratio of 1 acid to 60 rubber gives a rapid formation of a workable clot, but stronger doses may lead to a weak, flaky coagulum, which cannot be milled and only coheres slowly. Compared with crepe from undiluted latex, coagulated with a normal amount of acetic acid (1 gm per liter) and rolled after a few hours (so that in both cases no maturation takes place), the increase in acetic acid has the following result:

	Ordinary crepe	Trial coagulation
Cc. $2\frac{1}{2}$ % acetic acid per 100 cc. of latex	4	20
Time of cure	108	112
Slope	38	38
Viscosity	24	22

therefore in this case a small decrease in rate of cure and viscosity results.

If less acetic acid than the normal quantity is taken, this, strictly speaking, is a speculation upon the spontaneous formation of acid in the latex. With 0.3 — 0.6 cc. of acetic acid per liter of 15 % latex one can obtain a very good

coagulation, at least when the coagulum is left till the following day before milling. However the smaller the amount of acetic acid taken, the more the drawbacks of spontaneous coagulation — irregularity in the process, milky serum, formation of gas (bubbles) in the coagulum, and a yellow slime-layer on the surface, see § 94 — come into play. Since spontaneous coagulation (which, like the use of a small quantity of acetic acid, is excluded in the preparation of sheet rubber, and can only be employed in the preparation of crepe) gives only a 10 minutes shorter time of cure and a little (7 units) higher viscosity, the differences obtained by using less than the normal amount of acetic acid have also little or no practical significance.

For data on spontaneous coagulation see § 94—97.

K. GORTER and N. L. SWART (Med. W. J. No. 6 page 8, Agric. Bull. F. M. S. 4 (1916), 50) found that in a liter of latex, to which only 0.3 gm. acetic acid had been added, 0.8 gm. lactic acid and 0.23 gm. acetic acid had been formed in 24 hours, beside 0.08 gm. succinic acid.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 208) found no difference in rate of cure and tensile strength when crepe was prepared by slow, eventually incomplete, coagulation with small amounts of acetic acid (1 acid per 225 to 600 rubber).

Influence on chemical composition.

The chemical composition of the rubber does not change with the above mentioned variations in amount of acetic acid; it is only when very large doses are used that somewhat more protein seems to be precipitated with the rubber.

In the above mentioned experiments by L. E. CAMPBELL (l.c.) the resin-content of the unsmoked sheet showed no difference with the use of increasing amounts of acid, whilst the protein and ash in the rubber in only one case increased slightly with the use of more acid.

W. CROSSLEY (I R. J. 41 (1911), 1207), working with a strongly diluted (7 %) latex preserved with formalin, found the protein-content of the rubber to increase from 3.2 to 4 % for an increase of acid up to 15 or more times the normal amount, but for the ordinary amounts of acetic acid the difference was negligible.

A point of interest in coagulation with acids is, of course, the quantity of acid absorbed by the rubber. Though these absorption phenomena form a complicated problem, which has not been sufficiently studied, it may safely be assumed that the fear of a residuum of the acid used in coagulation has often been exaggerated. In Chapter XXI we give figures for the acidity of different types of rubber, which of course is partly due to the acids developed in the latex. In how far the acidity found in the watery extract of rubber is really caused by free acid in the rubber and in how far by decomposition during extraction, remains to be seen. From the figures in § 186 and Chapter XXI it will be seen that Brazilian rubber, coagulated without addition of acid, shows a higher acidity in the watery extract than well-washed plantation crepe. Figures on the acidity of rubber coagulated with increased amounts of acetic acid are scarce, and the question of the absorption of acid by the rubber may not yet be regarded as cleared up.

Ph. SCHIDROWITZ and H. A. GOLDSBROUGH (I.R.J. 44 (1912), 1147), in two series of experiments made by G. S. WHITBY, found the acidity of unsmoked sheet — which, by the way, was lower than is usually stated, see Chapter XXI — to decrease with increasing amounts of acetic acid.

§ 84. Other coagulants containing acetic acid.

The enormous rise in price of acetic acid in the beginning of the war was the cause of a search in every direction for substitutes. Amongst others the preparation of acetic acid by distillation of wood, and the fermentation of sugar or alcohol (or denatured spirit) were tried.

The dilute acetic acid which one obtains in this way has commonly a content of 3 to 7 %_v. As a coagulant the acid liquids so obtained may be satisfactory, and the properties of the rubber not inferior to those obtained by the use of pure acetic acid. The differences are often nil, though sometimes present, but insignificant, and it is only when wood-distillate insufficiently freed from tar is used that a distinct decrease in rate of cure is obtained.

An objection to the use of such dilute acids is that the strength of preparations from different days is not always the same, so that one would have to determine and regulate it (dilute to a fixed acid-content after titration), or else use such an excess that there is no danger of incomplete coagulation. Further the transport, at least over great distances, of such diluted acids is too costly.

For a group of neighbouring estates (or individually for large estates) it has been proved to be possible to erect a simple acetic acid distillation plant, in which tar and charcoal might constitute valuable by-products. The costs of transportation would then be small, and as the acid is cheap, a rather large portion could be used, to avoid incomplete coagulation when the acid is somewhat weaker than usual. In the wood-distillation, however, one has to take care that the tarry products are sufficiently removed, because they may produce a very dark colour in the rubber. The acid distillate from wood is, in general, unsuitable for the preparation of crepe, in which a slight darkening of the colour is so very noticeable. When smoked sheet is prepared, the danger is not so great, but still the darker colour of the sheets, caused by acid that was insufficiently purified, may lower the market-price of the product more than the gain in reducing the cost of the acid. The difficulty of separating the tar-products has proved a practical drawback in the use of this otherwise very cheap and rational manner of obtaining acetic acid.

The fermentation of sugar or alcohol, though practicable on an estate-scale, demands adequate care and attention, which has to be weighed against the relatively small saving in costs for acetic acid.

The trials in these directions, because of these drawbacks, have not lead to any generally accepted results, and the use of pure acetic acid is preferred by most or all estates. The saving in cost — at least with present prices — does not urge any great exertions in this direction, and the chance that the colour or exterior appearance of the product may be somewhat damaged by the substitute tips the balance in favour of the pure acid.

B. J. EATON and G. S. WHITBY (Agric. Bull. F. M. S. 5 (1917), 124; see also Bull. F. M. S. No. 27 (1918), 244) studied the preparation and effect of the acid distillate from wood, as well as of the acid liquid obtained by passing the gasses of slow burning wood through water. Though sometimes no deviation in rate of cure from samples coagulated with pure acetic acid was found, in other cases the phenol-bodies or smoke-constituents exercised their retarding effect to a certain, though usually small, extent.

Experiments on the preparation of a crude acetic acid by destructive distillation of coconut shells were made in Ceylon (see Trop. Agric. 45 (1915), 250); the acid was much cheaper than ordinary acetic acid, but not clear enough in colour to be used in the preparation of crepe.

A. J. ULTÉE (Arch. 2 (1918), 343 and 728) also studied the use of the acid distillate from wood such as Hevea or coffee. A sufficiently large plant to provide acid for the whole production was erected on a large estate. No difference in properties of the rubber was found when the distillate was sufficiently purified; but often the crude acid was tarry and darkened the colour of the sheets too much and also retarded the cure somewhat.

P. E. KEUCHENIUS (Arch. I (1917), 417; *ibid.* 3 (1919) 21) experimented with acetic acid prepared by fermenting denatured spirit on a scale large enough to supply the daily needs of an estate. The rubber thus prepared had exactly the same properties as when commercial acetic acid was used; but the use of pure acetic acid was preferred when prices were low enough, as being a simpler method.

O. DE VRIES (Arch. 4 (1920), 179 and 214) gave figures for a number of samples of smoked sheet and crepe prepared by purified and by crude wood-distillate, and by acid from the fermentation of alcohol; the differences in inner properties of the rubber, as compared with that prepared with pure acetic acid, were mostly negligible.

Chinese vinegar and other such preparations have also been tried in times when acetic acid was scarce. The properties of the rubber are not affected, but the price of these dilute acids (containing $2\frac{1}{2}$ to $7\frac{1}{2}$ % acetic acid) prohibits their use in ordinary times.

See B. J. EATON (Agric. Bull. F. M. S. 4 (1916), 321); B. J. EATON, J. GRANTAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 241).

Some acid fluids obtained from other sources will be treated in § 93.

§ 85. Miscellaneous methods of saving acetic acid.

a. The use of serum.

For saving acetic acid, serum from the foregoing day which is still acid may be used in the place of water for diluting the acetic acid or for bringing the latex to standard rubber content.

In crepe there is a danger of striping or of discolouration, but in sheet-rubber this method does very well and approximately half of the acetic acid can be saved in this way.

The serum of one day can be used on several subsequent days, so long as it has not become dark-coloured or decomposed. Finally one must begin a new series by coagulating one day's product with pure acetic acid only.

Serum alone often has not a coagulating power strong enough to coagulate the whole next day's product. For satisfactory coagulation it generally has to be added in an amount of 1 volume of serum to 2 volumes of latex, and this requires more serum than is obtained in ordinary practice, where the coagulum cannot be worked in tanks or pans to yield the greater part of the serum. Addition of some acetic acid to the serum is usually necessary.

It is interesting to note that the coagulating power of serum is only approximately half as large as its acidity, calculated as acetic acid, would lead one to expect. To what difference in composition of the serum this is due, and whether serum contains anti-coagulating substances, remains to be investigated.

On the use of serum on subsequent days, and on the addition of sugar to the serum which increases its acidity by fermentation, see A. J. ULTÉE (Arch. 2 (1918), 340).

On the use of serum after sugar-coagulation, either with or without renewed sugar-addition, see K. GORTER and N. L. SWART (Med. W. J. No. 6, page 11 and 22), who found the addition of an equal volume of serum to undiluted latex to produce coagulation in $1\frac{1}{4}$ hours, whilst half a volume gave coagulation in 4 hours. This serum after 18 hours regularly showed an acidity corresponding to 0.3% acetic acid.

G.S. WHITBY (Agric. Bull. F.M.S. 6 (1918), 378) states that the coagulating effect of serum is variable and not so great as its acidity would lead one to expect. Perhaps other substan-

ces, eventually anti-coagulating by-products, play a role. Serum from acetic acid coagulation with an acidity equivalent to 2.8 cc acetic acid per liter had to be added in an amount of at least 500 cc (that is 1.5 cc acetic acid) per liter of latex, or twice as much as in ordinary coagulation.

On the inner properties of the rubber the use of serum has little influence, as we will see in § 112.

The objections to this method — the necessity of straining small clots of rubber or of precipitated protein from the serum the slightly putrid smell which the serum takes on after some time; the only approximate knowledge of the acid-content — have caused it to be used only in times of need. The pure acid, which is clean and easy to dose, is preferred, especially as the saving in cost is relatively small.

A. J. ULTÉE (Arch. 2 (1918), 340), in experiments with smoked sheet and crepe, found no difference in properties of the rubber when the serum was used; the viscosity sometimes showed a small increase, sometimes a small decrease.

b. Heating the latex.

Some investigators have proposed to heat the latex somewhat as a means of saving acetic acid; for instance when the latex is heated to about 50° C a smaller quantity of acetic acid is necessary. As the heating of large volumes of latex is not simple, it depends on local conditions whether or not this method is feasible and gives a saving in cost.

The influence of this method of preparation on the inner properties of the rubber is not yet known (see however § 100 on coagulation by heat).

Cl. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 33; also Z. Koll. 13 (1913), 216) give figures for dialysed preserved latex (15% total solids), in which 1 cc acetic acid (added in the form of a 1% solution) gave coagulation in 20 seconds when the mixture was immersed in boiling water, whilst for 0.7 cc and 0.5 cc the time was 40 seconds, for 0.4 cc 65 seconds, 0.3 cc 5 minutes; 0.2 and 0.1 cc gave no immediate coagulation.

G. S. WHITBY (VIII. Int. Congr. 25, 606; also I.R.J. 45 (1913), 943; also Z. KOLL. 12 (1913), 152) found that even the small increase in acidity, caused by bubbling carbon dioxide through the latex, lowered the temperature of coagulation from 71 to 63°.

§ 86. Sulphuric acid.

During the time that acetic acid was scarce and expensive, sulphuric acid was used on some estates as a substitute. Dilute sulphuric acid gives a good coagulation and moreover has, to some extent, anti-oxydising properties. By its use, even without bisulphite, a sufficiently pale crepe can be obtained, though the colour of the fresh crepe has a somewhat greyish and not a pure white tint.

Calculated per volume, it has a stronger coagulating effect than acetic acid, so that, in proportion, less of it is needed: per liter of 15 % latex, for which 0.75 cc — 1 cc acetic acid is necessary, one has to add only $\frac{1}{4}$ cc — $\frac{1}{3}$ cc (0.45 gm — 0.6 gm) of strong sulphuric acid, for instance in the form a 1 % or 5 % solution.

For the inner properties of the rubber sulphuric acid is not so favourable. It decreases the rate of cure and the viscosity, while in larger quantities the tensile strength is also reduced. When the minimum amount is used, the difference between rubber coagulated with it and that with acetic acid is not of much importance, and such small quantities of sulphuric acid can be used without objection; but with larger quantities the harmful effects increase rapidly. This may form a serious drawback, because in ordinary estate practice, from one cause or another, a quantity of acid somewhat larger than the normal may accidentally be taken. With acetic acid this is of little importance in regard to the inner properties of the rubber (see § 83), but with sulphuric acid one obtains much more marked deviations by increasing the amount of acid, so that lack of uniformity is the result, and eventually a rubber which vulcanises abnormally slowly is obtained.

An idea of the effect of sulphuric acid on the inner properties of the rubber may be obtained from the following figures.

	Tensile strength	Time of cure	Slope	Viscosity
Acetic acid, normal quantity	1.41	120	38	35½
" " double "	1.40	125	38	34
Sulphuric acid, normal "	1.40	125	38	35
" " double "	1.36	150	38½	27

See O. DE VRIES, Arch. 4 (1920), 165 and 210, where figures are also given for crepe from an estate where sulphuric acid was in use, showing a rate of cure of 119 minutes, against 98 for the control (acetic acid in 15% latex). A larger dose of sulphuric acid (1 in weight to 22 rubber) gave a time of cure of 220 minutes, which is abnormally large.

S. MORGAN (Prep. Pl. Rubber (1913), page 223 and 230) mentions sulphuric acid as an efficient and cheap coagulant, but states that the disadvantages will usually outweigh the advantages. The resiliency, resistance to stretching and recovery were found to decrease with increased amounts of acid, indicating that sulphuric acid in larger amounts retards the cure.

B. J. EATON (Agric. Bull. F. M. S. 4 (1916), 165 and 7 (1919), 225; see further Bull. F. M. S. No. 27 (1918), 223) warned against the use of sulphuric acid, because it retards the rate of cure, and does this very markedly when used in more than the minimum quantity.

In experiments by L. E. CAMPBELL with unsmoked sheet (Bull. Ceyl. No. 23 (1915); Bull. Imp. Inst. 14 (1916), 502; *ibid.* 16 (1918), 412) no decrease in tensile strength or rate of cure was found when the minimum amount of sulphuric acid was used, but larger quantities retarded the cure markedly without altering the tensile strength or the chemical composition.

On the chemical composition of rubber coagulated with sulphuric acid data are scarce.

O. DE VRIES and W. SPOON (Arch. 4 (1920), 172 and 212) in one series of experiments found the moisture-content and acetone-extract to be the same as in the controls, but found the watery extract lower, and the ash higher in the sulphuric acid samples.

Whilst therefore sulphuric acid is not favourable to the properties of the rubber, a further point against its use is that

manufacturers have repeatedly shown a prejudice against rubber coagulated with such strong and corrosive acids. It may be assumed that the minimum amount of sulphuric acid does not harm the rubber; after being kept several years the rubber was found to have changed in properties in exactly the same manner as that coagulated with corresponding doses of acetic acid, and no special deterioration caused by sulphuric acid could be detected, unless unusual large quantities were used (such as $3\frac{1}{2}$ cc acid per liter of latex, or 1 acid to 22 rubber).

O. DE VRIES (Arch. 4 (1920), 165 and 210) in several series found samples of crepe and smoked sheet, kept for 1 to $3\frac{1}{2}$ years, to change in properties in the same way whether acetic or sulphuric acid was used. When minimum quantities were used, the tensile strength and viscosity decreased somewhat, and the rate of cure increased, as is generally found when raw rubber is kept (see § 163). Larger doses of acid gave a more marked decrease in tensile strength and viscosity, and in such cases the rate of cure of the sulphuric acid samples increased more rapidly than that of the controls, and even regained normal values, as if the original retarding substance gradually disappeared.

On keeping vulcanised samples (ordinary rubber-sulphur mixture, see Chapter XVII, § 198 and 209) for 3 to 152 days, the change in properties for the acetic acid and for the sulphuric acid samples were also the same.

Only when much too large doses of sulphuric acid were used, was a rubber with very low tensile strength, slow rate of cure and low viscosity obtained. This rubber showed a marked decrease in viscosity on keeping, without however becoming tacky.

In this connection it is interesting to note that G. S. WHITBY (VIII Int. Congr. (1912) 25, 617; also I.R.J. 45 (1913), 1043, and Z. Koll. 12 (1913), 191) found that rubber, which had been immersed for 18 months in 25 % sulphuric acid, did not become tacky when taken out of the acid and allowed to dry.

B. J. EATON (Agric. Bull. F. M. S. 7 (1919), 225) warned against the soaking of sheet-rubber in dilute sulphuric acid after machining (see § 195), as this treatment, although it gives an excellent outer appearance, gives a very inferior quality. This result was confirmed by a manufacturer's report from England.

It is further worthy of note that B. J. EATON and F. W. F. DAY, (J. S. Ch. I. 38 (1919), 339 T) found considerable amounts of sulphuric acid to be formed by oxydation in vulcanised rubber-sulphur mixtures, when they are kept in the air.

When the rubber is vulcanised in mixtures containing oxydes such as ZnO , MgO etc, traces of free acid, if indeed present, would be combined and made harmless.

W. ESCH (I. R. J. 48 (1914), 71) tested rubber coagulated with sulphuric acid in a mixture containing zinc oxyde, and found the vulcanisate inferior.

Perhaps, for special purposes, rubber coagulated with sulphuric acid may be less desirable; but no data are available to prove this, and the supposed harmful effect of sulphuric acid may be regarded as not well defined nor sufficiently known.

Sulphuric acid has in practice the drawback, that the strong concentrated acid, the well known vitriol, is a dangerous article and that, in diluting it with water, an enormous quantity of heat is developed; so that in unskilled hands it can give very disagreeable surprises. Further, the acid strongly corrodes the iron of the rolls, the floor of the factory etc.

From all these reasons sulphuric acid, at least in Java, never found much favour; and, though cheaper than acetic acid, it was used only exceptionally, while the small number of estates, which used it, dropped its use once acetic acid was again abundant and not unduly expensive.

L. MORISSE (Le Latex, page 224) proposed a mixture of sulphuric acid and phenol as a coagulant, but this has found no application in estate-practice.

§ 87. Formic acid.

Formic acid, as the acid most closely related to acetic acid, has repeatedly been recommended as a substitute; but so far as known, in Java it has not been applied on a practical scale. It is a good coagulant, which has a somewhat stronger effect than acetic acid; the ratio of strength may be taken as 3 (or a little more) to 4.

It may also have a good effect on colour, since it prevents oxydation (violet discolouration) to a greater extent than acetic acid, while, at least under favourable market conditions, it is also somewhat cheaper than acetic acid.

The effect on the inner properties of the rubber has not yet been fully explained. In many cases one finds no deviation from samples for which acetic acid was used, but in others the rate of cure and viscosity are reduced by the use of formic acid, sometimes to a very noticeable degree.

It is likely that the formaldehyde-content in formic acid may offer an explanation, but this will have to be further investigated. The uncertainty of its effect is an objection, which causes acetic acid to be preferred in estate-practice.

C. O. WEBER (*Trop. Agric.* 23 (1904), 654) already mentioned formic acid as a good coagulant, of which three parts have the same effect as four parts of acetic acid.

D. SPENCE (*I. R. J.* 35 (1908), 426) found the physical properties and the chemical composition of rubber coagulated with formic acid nearly the same and quite as good as when acetic acid was used, whilst less of it (only half the amount) was necessary, and its antiseptic action helped to keep the rubber pale and in good condition.

S. MORGAN (*Prep. Pl. Rubber*, page 218) found formic acid a good coagulant, which, when used in minimum quantities (0.8 cc. per liter undiluted latex), gives a rubber of the same physical qualities as acetic acid. Taking into account all factors (strength of commercial acid, coagulating power, costs) no difference was found in favour of one acid or the other.

S. RIDEAL (*Proc. III^d Congr.* 1914, 147) recommended formic acid because it is a disinfectant, and because if it undergoes changes it forms carbonic acid and no residue is left in the finished rubber.

In experiments made by L. E. CAMPBELL (*Bull. Ceyl.* No. 23 (1915); *Bull. Imp. Inst.* 14 (1916), 502; *ibid.* 16 (1918), 412) an increase in amount of formic acid was found to retard the cure (for the double amount with 15 to 40 %), whilst the influence of formic acid on tensile strength and chemical composition was nil.

K. GORTER and N. L. SWART (*Med. W. J.* No. 6, 17) mention that 2 parts of commercial 90 % formic acid have the same coagulating effect as 3 parts of acetic acid.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (*Bull. F.M.S.* No. 27 (1918), 232) found the effect of small doses on slab-rubber to be insignificant, so that in ordinary sheet or crepe also there is no marked difference in rate of cure to be expected between acetic and formic acid when 0.5 gm — 0.6 gm of the latter per liter of latex is used.

O. DE VRIES (*Arch.* 4 (1920), 206 and 218) mentions several cases in which the minimum dose of formic acid

gave rubber of the same properties as acetic. With increased amounts of formic acid, however, the rate of cure decreased more rapidly than with acetic acid, and in some cases even a small dose of formic acid gave a rubber which vulcanised slowly. The differences in tensile strength and slope were unimportant, the changes in viscosity were parallel to those in rate of cure.

On keeping the raw rubber, the changes in one experiment were found the same as after coagulation with acetic acid.

§ 88. Alum.

Alum is one of the oldest coagulants, in sufficient doses having a strong coagulating power. As in the East it is obtainable everywhere as a cheap powder, it is a very handy coagulating medium for small native holders.

See for instance on its use in Brazil, P. CIBOT, J. d' A.T. 3 (1903), 37, and H. C. PEARSON, Rubber Country of the Amazon, page 73 and 171.

In spite of the fact that warning against the use of alum as a coagulant has been given for years from all quarters, this substance is still often used by native planters. On European estates it was, as far as is known, used only in the time of shortage of acetic acid.

See for instance the old warnings in Seeligm. (1896), page 64; P. VAN ROMBURGH, Med. Pl. 39 (1900), 36.

On measures taken by the F. M. S. Government to prohibit the use of alum, see Agric. Bull. F. M. S. 7 (1919), 224 and 242.

Alum is harmful to the inner properties of the rubber; but the casual observer is not inclined to suppose or believe so, because the coagulum, especially when a large quantity of alum is used, becomes very stiff, and looks as if it were very strong.

In coagulation, 3 or 4 gm. per liter of latex are necessary. Compared with acetic acid this quantity, and larger doses, may give about the following differences in the inner properties of crepe-rubber.

	Alum per liter of latex		
	3 — 4 gm.	10 gm.	20 gm.
Increase in time of cure	15 min. and more	30 and more	85 and more
Decrease in viscosity	4 — 7	7 — 12	10 — 12

With the ordinary quantity of alum, the differences are very noticeable, and with larger quantities the inner properties of the rubber are greatly injured; especially the rate of cure becomes very low, and may attain such abnormal figures as 200—240 minutes, which are found with only a few coagulants (compare § 86 and 91).

B. J. EATON, (Agric. Bull. F. M. S. 6 (1918), 316 and 422; *ibid.* 7 (1919), 224) found alum to retard the cure greatly, and the rubber of native holders, coagulated with alum, to show a very large variability in rate of cure. Various alum salts, other than the usual potassium salt, had the same effect in retarding the rate of cure.

O. DE VRIES (Arch. 4 (1920), 173 and 213) found the use of alum to cause the above mentioned changes in rate of cure and viscosity. The tensile strength was not found to decrease more than might be expected because of the much prolonged time of cure, whilst the slope decreased somewhat (became better) by using this coagulant.

S. MORGAN, F. W. F. DAY and H. P. STEVENS (Bull. R. G. A. 2 (1920), 142) found that 2½ gm. of alum per liter of latex gave 10% decrease in rate of cure against acetic acid controls; but when using the same amount in latex, to which sulphite had been added as an anti-coagulant (so that the dose of alum was not wholly sufficient and the serum milky), the difference in rate of cure was negligible.

Soaking a piece of dry crepe in an alum solution was found by O. DE VRIES (Arch. 2 (1918), 93 and 103) to retard the rate of cure and decrease the viscosity. In this case the alum can act only as a chemical, a negative catalyst.

When crepe and sheet prepared with alum are kept, the properties do not show any marked deterioration, and do

not change more than those of rubber prepared with acetic acid. In contrast to such coagulants as sulphuric and hydrochloric acid, alum does not seem to cause any slow deterioration or decomposition of the rubber, and its harmful effect is only the direct, probably catalytic, decrease in rate of cure and viscosity, by which a rubber which is abnormally slow in vulcanisation is produced.

See O. DE VRIES, Arch. 4 (1920), 177 and 213.

It may further be mentioned that large quantities of alum prevent surface-oxidation (violet discolouration) and keep the coagulum perfectly white. The rate of drying of the rubber is markedly retarded by the use of this coagulant.

See O. DE VRIES, Arch. 4 (1920), 174 and 213.

That alum is absorbed by the rubber during coagulation, can often be proved by the increased ash-content, which from the ordinary figure of 0.2 % to 0.3 % may increase to 0.6 % or even 0.9 %, depending on the amount of alum used, whether the preparation is in the form of crepe or of sheet, etc.

See O. DE VRIES, Arch. 4 (1920), 175 and 213.

It is interesting to note that the effect of alum on rate of cure and viscosity is the same in crepe as in sheet, even when the crepes are very thoroughly washed with water, and the sheets rolled without using water. The retarding substance, once incorporated in the rubber during coagulation, does not seem to be washed out again. In the same way, soaking the coagulum prepared with alum for one night in water before rolling does not increase the rate of cure or the viscosity.

See O. DE VRIES (Arch. 4 (1920), 177 and 213). It may be remarked that the ash-content of the crepes was regularly found to be somewhat lower than that of the sheets, whilst the time of cure was even somewhat greater.

Drying the sheets at elevated temperature gave a somewhat larger time of cure than drying at room-temperature.

§ 89. Mineral acids.

Hydrochloric acid.

Hydrochloric acid has a strong coagulating effect, but has been found less favourable to the properties of the rubber, and as a strongly corrosive acid is condemned by manufacturers. Moreover it gives a regular coagulation only within narrow limits. Larger doses of this acid leave the latex (at least when it is diluted) fluid, whilst still larger quantities produce immediate clotting. The safe range for coagulation with small amounts is smaller than with other acids. The ranges of dilution and amount of acid added, in which no coagulation takes place, have however not yet been worked out sufficiently.

S. MORGAN (Prep. Pl. Rubber, page 216 and 233) indicates 0.7 cc HCl per liter of undiluted latex as a suitable dose for coagulation, so that the costs would be the same as for acetic acid. He found the resiliency, resistance to stretching and recovery, for samples coagulated with hydrochloric acid, lower than normal, indicating a small rate of cure.

B. J. EATON, J. GRANTHAM and F.W.F. DAY (Bull. F.M.S. No. 27 (1918), 228) found that hydrochloric acid retards the cure of matured rubber markedly

O. DE VRIES and H. J. HELLENDORF (Arch. 4 (1920), 209 and 219) found a strong dose of hydrochloric acid to retard the rate of cure greatly, though not so much as a corresponding dose of sulphuric acid. Tensile strength and viscosity were also markedly injured, but the slope decreased somewhat (became better). After being kept for two years the sample of crepe became completely tacky, and the viscosity decreased to very low values.

G.S. WHITBY (VIII Int. Congr. 25, 612; also I.R.J. 45 (1913), 945, also Z. Koll. 12 (1913), 156; further Agric. Bull. F.M.S. 6 (1918), 381) found that no coagulation took place when between 3 cc and 10 cc of 10% hydrochloric acid were added per liter of 10% latex.

B. J. EATON (Bull. F.M.S. No. 17, 12) found incomplete coagulation also in undiluted latex, when using dilute acid. He found the limits, between which coagulation is incomplete, to depend partly upon the dilution in which the acid was added.

Hydrofluoric acid (Purub).

Purub, a solution of hydrofluoric acid, was much advertised some years ago. It was claimed, besides being

a good coagulant, to produce, as a disinfectant, a very pure and stable rubber of light colour.

See for instance G. SANDMANN (Agric. Bull. Str. F. M. S. 8 (1909), 111); and F. FRANK, (G. Ztg. 22 (1908), 1404). Further F. FRANK and E. MARCKWALD (Lectures 1908, page 178; I. R. J. 36 (1908), pages XIII, 320 and 412).

S. MORGAN (Prep. Pl. Rubber, page 216 and 224) mentions that undiluted latex is coagulated by 0.5 cc hydrofluoric acid per liter, but the costs are much higher than with acetic acid, and the claim that the rubber is superior was refuted.

It seems that this coagulant is of some importance in the coagulation of latices other than Hevea, for instance in latices of the African colonies. On Hevea-plantations in the East it has not found favour, in the first place because it is too expensive, and in the second place because its application is not without objections, as it is corrosive, volatile, and attacks silicates, making it impossible to keep it in glass vessels.

The properties of the rubber are not affected to any great degree by this coagulant; the rate of cure may decrease somewhat, especially with large doses, but the tensile strength generally remains the same as for rubber coagulated with acetic acid. The chemical composition of the rubber is normal.

See the experiments by L. E. CAMPBELL (Bull. Ceyl. No. 23 (1915), page 2 and 12; *ibid* No. 24 (1915), page 3; Bull. Imp. Inst. 14 (1916), 502 and 507; *ibid* 16 (1918), 412).

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 229) found the rate of cure of matured rubber to be decreased by the use of hydrofluoric acid, whilst the tensile strength was unaffected.

Nitric acid.

Nitric acid also has never attracted much attention and does not seem a suitable coagulant, as the properties of the rubber are injured by it. It shows the same phenomenon as hydrochloric acid of leaving the latex uncoagulated when added in a certain not too large amount.

S. MORGAN (Prep. Pl. Rubber, page 216 and 233) found that nitric acid gave a coagulation in an amount of 1 cc per liter of undiluted latex, and calculates the cost as somewhat cheaper than that of acetic acid. He stated that nitric acid gives very low figures for resiliency, resistance to stretching and recovery, so that the rubber apparently cured very slowly.

B. J. EATON (Bull. F. M. S. No. 17, page 13) and G. S. WHITBY (Agric. Bull. F. M. S. 6 (1918), 381) gave figures for the range over which coagulation with nitric acid is complete or incomplete.

Sulphurous acid.

Sulphurous acid may be used as a coagulant, and suggestions or patents involving its use have appeared from time to time. It would constitute a cheap coagulant, at the same time saving the cost of bisulphite, as the anti-oxysing action of the sulphurous acid is sufficient. The gases from burning sulphur may be sucked through the latex, in which case however an irregular clotting takes place at the point where the gases enter into the latex. Again these gases might be dissolved in water to form a dilute solution, which then might be dosed and diluted to a fixed content, to obtain a regular coagulation. Of course, liquid SO_2 from bombs might also be used, for instance to make a dilute solution, but this would be somewhat more expensive.

As we stated in § 52, sulphurous acid in normal quantities has no effect on the rate of cure of the rubber, whilst tensile strength and viscosity increase somewhat, and the slope decreases (becomes better). The rate of drying of the rubber, however, is somewhat decreased.

See O. DE VRIES, Arch. 2 (1918), 94 and 113.

On a patent apparatus for coagulating with vapours of burning sulphur see I.R.J. 57 (1919), 319. The rubber coagulated by this process was found several times to cure slower than the control, whilst the rate of cure varied considerably from day to day. The tensile strength was the same, the viscosity somewhat higher, the slope 2—3 units lower (better) than in the control. The coagulation was often incomplete, owing to the formation of clots where the gases entered the latex, so that coagulation with acetic acid was preferred as simpler and giving a better and more uniform product.

The use of sulphurous acid in bombs was discussed by S. MORGAN (Prep. Pl. Rubber, page 225), who found good coagulation to occur when between 8 cc and 15 cc of a 1% solution per 100 cc latex of 21% rubber were added, so that the limits, within which good coagulation is obtained, are rather narrow.

Though, probably, sulphurous acid might form a cheap and good coagulant, the difficulties connected with its preparation and the dosing of its solutions have checked its use, and as far as known, it has never been used in estate-practice other than on an experimental scale.

Carbon dioxjde.

Carbon dioxjde, when bubbled through the latex, causes some clotting or coagulation, which however is not complete. Its effect is of a certain importance, as this gas is formed in large quantities during spontaneous coagulation. But the theory, once propounded with much enthusiasm, that carbonic acid would play the principal role in coagulation in the Brazilian method, was never satisfactorily proved, and seems to find no support in any facts known at the present time.

No data have been published on its effect on the properties of the rubber; its influence may be supposed to be small.

See S. MORGAN, Prep. Pl. Rubber, page 217; B. J. EATON Bull. F. M. S. No 17, 35; W. PAHL, Rubb. Ind. 1911, page 234; I. R. W. 45 (1912), 211; C. Gp. 1911, page 5496.

Other acids.

A large number of other acids have been tried as coagulants. Amongst them we may mention *molybdc acid* and *phosphotungstic acid*, well known protein-precipitants.

These acids greatly retard the rate of cure, and this is due to a direct action as negative catalysts. When the acid is added to dry rubber before vulcanisation, the same retarding effect is produced.

B. J. EATON, Agric. Bull. F.M.S. 6 (1918), 423; *ibid.* 7 (1919), 225.

G. S. WHITBY (Agric. Bull. F. M. S. 6 (1918), 379), in a preliminary experiment, found phosphotungstic acid to produce a flocculent precipitate and not a coherent clot.

Acids that inhibit coagulation.

It is interesting to state that of some acids it is mentioned that they do not coagulate latex. So for instance *boracic acid*, *hydrogen sulphide* and *hydrocyanic acid*.

See for boracic acid B. J. EATON, Bull. F. M. S. 17, page 22; for hydrogen sulphide G. S. WHITBY, VIII Int. Congr. 25, 605. also I. R. J. 45 (1913), 943, also Z. KOLL. 12 (1913), 152.

§ 90. Salts.

The fact that salts in general have an influence on coagulation, has already been discussed in § 74 and 75: coagulation by acids is often furthered by the addition of salts, and even the salts naturally present in latex play a role which is often under-estimated, and probably gives the explanation of certain differences between diluted and undiluted latex.

Apart from this effect of salts in general as additional substances, many salts are direct coagulants, though often rather large quantities are necessary to obtain complete coagulation. We will mention only a few of them as examples. None of them has any importance in actual practice, except alum, which was discussed in § 88.

Sodium bisulphate.

This salt, also called "nitre cake", which is obtained as a by-product in different industries, has been recommended as a cheap coagulant in case of necessity. One uses about $1\frac{1}{2}$ gm. per liter of 15 % latex, and it is cheaper than acetic acid. In its effects on the inner properties it somewhat resembles sulphuric acid, but the differences between its effect and that of acetic acid are not very great and perhaps in some cases this salt might be used as a substitute.

Sodium sulphate.

That sodium sulphate, added in quantities of 1 gm. — 4 gm. per liter of latex, is without effect on the properties of the rubber, was noted in § 52. This neutral salt also has a coagulating effect, but to a much lesser degree than the acid bisulphate.

C. O. WEBER (Trop. Agric. 23 (1904), 653) described a method to obtain a rubber free from albuminous matter by first adding 6 cc of formalin per liter of latex, and then 125 cc of a boiling 10% solution of sodium sulphate. He called the separation so obtained coalescence, as distinct from coagulation in which proteins play a role.

G. S. WHITBY (VIII Int. Congr. (1912), 25, 611; also I. R. J. 45 (1913), 945, and Z. Koll. 12 (1913), 155; further Agric. Bull. F. M. S. 6 (1918), 379) found that hot solutions of sodium sulphate produce a flocky precipitate, giving a rubber with no less than 1.49% ash.

N. W. BARRITT (Rubb. Ind. 1914, 130 and I. R. J. 48 (1914), 71; further J. S. Ch. I. 33 (1914), 289, also I. R. J. 47 (1914), 752) gave some figures on the influence of this salt on coagulation with sulphuric and acetic acid.

Sodium chloride.

Common salt has long been known as a coagulant, but it is effective only in rather large quantities. Some 8 gm. to 12 gm. per liter of undiluted latex have to be added, and dilution of the latex makes coagulation much more difficult or even impossible. In practice the coagulation is not reliable enough, and the quantities necessary are too large, so that this cheap and easily obtainable substance has no importance as a coagulant.

On the properties of the rubber the influence is not favourable. The inner properties show but little change, the rate of cure and viscosity decreasing somewhat; but the rubber dries very slowly and when in the form of sheet is difficult to dry.

See also B. J. EATON, Bull. F. M. S. No. 17, page 24.

J. PARKIN (Ann. Bot. 14 (1900), 197) mentions that sodium chloride never causes coagulation in diluted latices, the serum always remaining milky.

Calcium chloride.

Calcium chloride may be quoted as an example of a salt with a stronger action, which in undiluted latex gives rapid coagulation in an amount of 1 gm., whilst $\frac{1}{4}$ to $\frac{1}{2}$ gm. are sufficient for ordinary coagulation. In dilute latex, however, coagulation is not so easy and the effect on undiluted latex is not always the same, probably because of changes

in rubber-content. The relations between the dilution of the latex and the amount of calcium chloride necessary to give immediate or gradual coagulation deserve further study.

In how far the properties of the rubber are affected, is not yet known.

See f. i. L. E. CAMPBELL, J. S. Ch. I. 36 (1917), 274.

G. S. WHITBY (VIII Int. Congr. 25, 609; also I. R. J. 45 (1913), 944, also Z. Koll, 12 (1913), 154) found that in 12% latex 5 gms of calcium chloride per liter are necessary to cause coagulation. He remarked that this salt has a marked influence on the tendency to oxydation: using 10 gms per liter 12% latex, the violet discolouration was already visible after 20 minutes.

Small amounts of calcium chloride may encourage spontaneous coagulation (see § 97).

Other salts.

A large number of other salts have been tried as coagulants, but none of them has any practical importance, and it does not seem worth while to mention the scattered data about them that may be found in literature.

Though most salts either coagulate, or help coagulation by acids, some salts directly inhibit natural coagulation, probably because they act as disinfectants and hinder the growth of acid-forming bacteria. Among such salts may be named *potassium oxalate*, *sodium fluoride* and *potassium cyanide*.

See M. BARROWCLIFF (J. S. Ch. I. 37 (1918), 49 T) and G. S. WHITBY (Agric. Bull. F. M. S. 6 (1918), 380).

L. E. CAMPBELL (J. S. Ch. I. 36 (1917), 275) ascribed the effect of potassium oxalate and sodium fluoride to a precipitation of the calcium salts naturally present in latex, which calcium salts, he supposed, stimulated enzymic action. -

It is interesting to note that another well known disinfectant, viz. mercuric chloride (corrosive sublimate) is a coagulant, and was one of the first to be proposed as such, as J. PARKIN (Circ. R. B. G. 1 (1899), 152; Ann. Bot. 14 (1900), 197; I. R. J. 36 (1908), 459; Trop. Agric. 35 (1910), 7) found it effective for dilute latices and recommended the use of 3 gms per liter of latex.

§ 91. Acid natural water.

As a rather curious instance of a coagulating medium, which however proved unsuitable for practical use, we may mention that in the beginning of the war, when in Java a scarcity of acetic acid seemed imminent, an energetic planter made experiments with the acid water from the Kawah Idjen, a large crater-lake in the East of Java, of which water enormous quantities would be available. This water contains a fairly large amount of alum, and also sulphuric and hydrochloric acid, so that it has a strong coagulating effect, whilst it yields a rubber of pale colour. This water is of varying strength, in proportion to the amount of rain that has diluted the upper layers of the lake, and in proportion as it is scooped from the surface or from the deeper parts, the acid springs being situated somewhere in the bottom of the lake. The acidity of the water in some samples taken from the surface of the lake varied from 0.4 to 1.5 normal; the composition was:

	I	II	
Dry substance . .	2.7	7.5	gm. per 100 cc.
Ash	1.3	3.1	" " "
Acidity	0.4	1.5	normal
Hydrochloric acid.	0.6	—	gm. per 100 cc.
Sulphuric acid . .	1.75	—	" " "

Alum, sulphuric acid and hydrochloric acid, as we have seen above, are not without danger when used as coagulants. Used in very small quantities they yield a rubber which has approximately normal properties, but with larger quantities the quality of the rubber is greatly injured. The acid water from this crater-lake was therefore from the beginning regarded with suspicion, and was never used except for our experiments. Besides, the cost and the difficulties of transportation of such a dilute and corrosive acid liquid, which for instance will attack kerosene-tins, form a very considerable, if not unsurmountable, objection.

As an example of how large the changes caused by such coagulants may be, the following figures may be quoted for crepe coagulated with this medium, as compared with ordinary crepe coagulated by acetic acid.

	Decrease in tensile strength	Decrease in time of cure	Decrease in slope	Decrease in viscosity
Crater-water, minimum quantity	0.00	0 — 10	0	4
Same, double quantity . .	0.03	40	0	6
„ , quadruple „ . .	0.20	70	1 — 2	12 — 18.

These figures hold for crepe, tested a few weeks after preparation. It will be seen that, when more than the minimum quantity is used, the rate of cure and the viscosity of the rubber decrease very markedly, whilst the tensile strength is also injured. The slope, however, decreases (improves) somewhat.

Large quantities of such a corrosive coagulant have a strong deteriorating effect on stored rubber even in the case of crepe-rubber, from which the coagulant has been for the greater part washed out. When kept for one year, the raw rubber coagulated with a minimum amount of crater-water shows much greater deterioration than after coagulation with acetic acid, as the following figures may show.

	Tensile strength	Standard time of cure	Slope	Viscosity
Coagulated with acetic acid, fresh.	1.36	120	37	27.5
Coagulated with acetic acid, stored 1 year.	1.25	110	37.5	27.5

	Tensile strength	Standard time of cure	Slope	Viscosity
Coagulated with minimum crater-water, fresh. . . .	1.33	120	37	23
Coagulated with minimum crater-water, stored 1 year.	1.13	120	36	19.5
Coagulated with threefold quantity of crater-water, fresh	1.37	165	34.5	14
Coagulated with threefold quantity of crater-water, stored 1 year	1.18	160	37	12.5

It is clear that such a coagulant is unsuitable for use on estates; and we have mentioned its effects only as a curiosity, and to give a striking example of how the properties of the rubber may be injured, and may deteriorate on keeping, when the rubber is prepared in other than the recognized ways.

We may add that samples of crepe, prepared with a larger amount of this acid water, became completely tacky after 2 years keeping, whilst the colour changed from light yellow to a deep purple red, whilst the sample had become soluble in acetone for a great part (38—55 %). The crater-water, as was to be expected for a coagulant containing alum, gives a crepe with a higher ash-content than normal (0.4 to 0.6 instead of 0.2 to 0.3 %).

See O. DE VRIES, Arch. 4 (1920), 193, 197 and 216.

§ 92. Organic acids.

Since acetic acid was found so highly satisfactory for coagulation, a number of closely related organic acids have been tried and investigated.

Except formic acid, treated in § 87, none of them ranks among practically useful coagulants, but some of them are interesting in other respects.

Oxalic acid.

Oxalic acid is a good coagulant, and when used in not too small quantities gives a pale colour to the crepe; but it has no special advantages over acetic acid.

On the properties of the rubber it seems to have little influence, but experimental data — as, by the way, for other organic acids also — are rather scarce.

S. MORGAN (Prep. Pl. Rubber, page 216 and 224) found $1\frac{1}{4}$ gm. per liter of undiluted latex sufficient for coagulation, and calculated the costs as lower than for acetic acid.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F.M.S. No. 27 (1918), 235) found oxalic acid to give a pale rubber. Used in the preparation of slabrubber it gave a product of the same properties as when acetic acid was used.

Lactic acid.

As we will see in § 94 — 96, the natural acidity of latex is chiefly caused by lactic acid, formed by bacteria. This acid has also been tried as a coagulant, and was found to give rubber of practically the same properties as acetic acid. It is however much more expensive, and did not find application in practice.

See O. DE VRIES and W. SPOON, Arch. 4 (1920), 208 and 218, who found the rate of cure to be retarded to a small degree, whilst the other properties remained unchanged, and the crepe, on being stored for one year, altered in the same way as the controls prepared with acetic acid.

In one experiment by L. E. CAMPBELL (Bull. Imp. Inst. 16 (1918), 413) lactic acid did not cause marked differences in properties or composition of the rubber, as compared with acetic acid.

Tartaric acid.

This acid has also been tried repeatedly as a coagulant, but has nothing to recommend itself above acetic acid, and would be more expensive in use. On the properties of the rubber the influence seems to be small.

S. MORGAN (Prep. Pl. Rubber, page 216 and 227) found coagulation in undiluted latex to occur with $1\frac{3}{4}$ gms. per liter, so that the costs would be much higher than with acetic acid.

The acid seemed to retard the cure somewhat, but the difference between small and large quantities was not of importance.

B. J. EATON (Agric. Bull. F. M. S. 6 (1918), 148) found tartaric acid a suitable coagulant, but too expensive. Used in the preparation of matured rubber (Bull. F. M. S. No. 27, page 236), it gave the same results as acetic acid.

Citric acid:

The effect of citric acid is of some importance in explaining the action of fruit juices and such saps, treated in § 93, which mostly contain this acid.

Citric acid is a weaker coagulant than acetic acid, and more expensive; the properties of the rubber do not seem to be affected by its use.

S. MORGAN (Prep. Pl. Rubber, page 216) mentions that for 1 liter of undiluted latex 1.8 gm of citric acid are necessary, so that this coagulant would be too expensive for practical use.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 233) found citric acid to have the same effect in the preparation of slabrubber as acetic acid.

Tannic acid.

Tannic acid is of special importance, because it is a strong protein-precipitant. It gives flocculation in latex; in the serum obtained after ordinary coagulation with acetic acid it also gives a precipitate of substances which were left in solution during acetic acid coagulation. On its influence on the properties of the rubber few data are available.

C. O. WEBER (Trop. Agric. 23 (1904), 654) obtained an excellent coagulation with tannic acid.

G. S. WHITBY (Agric. Bull. F. M. S. 6 (1918), 379), working with diluted latex, found coagulation by tannic acid to be characterised by the non-coherence of the coagulum and by the rapidity of coagulation. 4 gm of tannic acid were sufficient to flocculate a liter of 12.4% latex in 4½ hours, and 6 gm. to precipitate all precipitable matter from the serum also.

WHITBY obtained non-coherent coagula also with aqueous extracts of mangrove bark and gambier.

E. FICKENDEY (Z. Koll. 9 (1911), 82) added 10 gms of tannin per liter of latex, or a smaller quantity, and further acetic acid to obtain coagulation. He holds that the tannin protects the rubber against tackiness.

B. J. EATON (Agric. Bull. F. M. S. 6 (1917), 148 and 423) found that tannic acid, when added to the dry rubber before vulcanisation, retards the rate of cure.

The action of tannic acid and derivatives is further important, because ordinary latex is always to some degree mixed with the saps from cells and vessels, other than the latex-vessels, which have been opened by tapping. About the influence of the substances which come into the latex in this way, very little is known; but they may play a role in natural coagulation on the tapping cut (tree-scrap, see § 181), whilst either the original cell saps, or the watery extract of bark, may be to some extent responsible for lump-formation, especially on rainy days.

See G. VERNET, Bull. Mars. 1 (1919), 111.

§ 93. Acid saps and juices.

In the course of time a number of acid saps and juices have been tried as substitutes for acetic acid, for example:
fermented sugar water,
sour coconut milk,
fermented coffee-juice,
fermented cacao-juice,
fermented pine-apple juice,
and also the acid juices of several local fruits, and a number of other liquids.

These liquids contain organic acids such as citric acid, tartaric acid, lactic acid, acetic acid and others, which, as we have seen in § 92, are good coagulants. The inner properties of the rubber are seldom affected to any marked degree by these acids or by the other constituents contained in the saps, and the objections to their use are mainly of a practical nature.

The content of acid in the saps is usually unknown; it may vary from day to day, and on keeping generally decreases. This is in so far not a great objection, as one can allow a wide margin and use somewhat more of these cheap acid liquids than is strictly necessary.

A great difficulty in the general application of these

coagulants are the costs of transportation, which for these diluted acids soon become too large.

Also one must take into account that in some cases the colour of the rubber is affected, either because the saps themselves contain colouring matters, or because the constituents of the saps give rise to a more rapid decomposition in the coagulum and to the quick formation of a slimy yellow surface layer. In the preparation of crepe these difficulties have a prohibitive effect sooner than in sheet.

Furthermore these liquids do not fulfill some of the other desiderata enumerated in § 81: for instance they are often obtainable only in limited quantities. For large estates, where everything must proceed regularly and rapidly, one will naturally prefer the acetic acid, which can be secured in large quantities of constant composition.

Fermented sugar water.

Dilute sugar-solutions, when kept for some time, or infected with already fermented liquid, develop acidity. This liquid has been tried as a substitute for sugar coagulation (see § 96). It has the advantage over sugar-coagulation in that it can be used in the preparation of smoked sheet, as the formation of gasbubbles is not to be feared when adding the already fermented liquid to the latex.

The properties of the rubber are not affected, and the method is practicable, though with the objections mentioned above.

A. J. ULTÉE (Arch. 2 (1918), 337) found the viscosity of smoked sheet and crepe prepared with a fermented solution of sugar in serum of the foregoing day to be somewhat lower than for the control prepared with acetic acid.

Fermented coconut milk.

The water or the milk from the coconuts, if kept shut off from the air (for example in large flasks), gives an acid liquid of 0.08 to 0.11 normal in a few days, which in degree of acidity is therefore about as strong as 0.5 % acetic acid, and has a somewhat stronger coagulating effect. This liquid may be a very useful coagulant. The above mentioned

degree of acidity is reached in about 5 days and, when the liquid is kept in closed flasks, undergoes almost no change in several weeks.

If however coconut-milk is kept in contact with the air, only a lower degree of acidity is reached, which moreover quickly diminishes and then corresponds, for instance, with only 0.05 % acetic acid.

See O. DE VRIES, Arch. 4 (1920), 184 and 214.

For a good coagulation, about 150—250 cc of liquid fermented in flasks is necessary per liter of undiluted latex, whilst a sufficient amount of water may be added to bring the final mixture to a rubber content of 15 %.

The inner properties of the rubber are the same as after acetic acid coagulation, and in a long series of experiments we found the uniformity not less than in ordinary standard preparation.

The rate of cure and viscosity remained the same, even when the amount of fermented sap was considerably increased.

See O. DE VRIES, Arch. 4 (1920), 186 and 215.

Fermented coconut-milk is by far the best of all substitutes for acetic acid, and especially for native rubberplanters would be easy to procure, and is much more to be recommended than alum.

An objection is found only in the increased tendency of the coagulum to form a yellow surface-layer, which causes streaks in the crepe. Further the application of this method can only take place locally, as otherwise the costs of transportation are too high.

This coagulant has been used for a considerable period in the preparation of sheetrubber on estates with both rubber and coconut plantings.

K. GORTER and N. L. SWART (Med. W. J. No. 6 page 20, see also Agric. Bull. F. M. S. 5 (1916), 52) found the sugar-content of the milk from young nuts to be 5 %, so that a liquid containing 2.5 % acetic acid might be obtained after alcoholic and acetic acid fermentation. The actual acid-content

after fermentation in the air was only 0.4% after 7 days, and 0.46% after 15 days. Half of the acid formed was acetic, the other half lactic acid. The viscosity of smoked sheet prepared with this coagulant was the same as in sheet prepared with acetic acid.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S., No. 27 (1918), 239), in a few experiments, found the properties of the rubber to be approximately the same as after coagulation with acetic acid.

A. J. ULTÉE (Arch. 2 (1918), 337), in some experiments, found the viscosity of smoked sheet to be lowered by using this coagulant.

For experiments with coconut-water concentrated by evaporation to $\frac{1}{5}$ its volume, see O. DE VRIES, Arch. 4 (1920), 188 and 215. The acidity was 0.2 normal, corresponding to 1.2% acetic acid, but the coagulating power was the same as of 2½% acetic acid. The properties of the rubber were normal, but the cost of the acid, due to the transportation over long distances, was still much too high to replace acetic acid.

Fermented coffee-juice.

By this name is meant the acid liquid which is obtained by soaking and fermenting the red coffee berries in water for some days. This extract has properties similar to these mentioned above, but contains a red colouring matter which in sheetrubber produces a darker red tint than usual, and colours the crepe dark reddish brown. The inner properties of the rubber also appear to be somewhat injured.

Since this acid is obtainable only during the coffee harvest, that is, during a few months of the year, it would only be available as a substitute in special circumstances, and cannot compete with other possible substitutes for acetic acid treated in this Chapter.

A. J. ULTÉE (Arch. 2 (1918), 336) found the viscosity of a sample of smoked sheet to be somewhat decreased by the use of this fluid. In some samples we found the properties after vulcanisation to be somewhat worse than after preparation with acetic acid (see Arch. 4 (1920), 191 and 216).

The same may be said of *fermented cacao-juice*, by which is meant the sour liquid dripping from fermenting cacao, with which trial coagulations have also been made.

A number of other saps and juices have been tried and experimented with, such as extracts from tamarind, mango-steen etc, or fermented pineapple-juice and the like. All such liquids are useful coagulants when nothing else is available, and certainly are to be preferred to harmful substances such as alum. Under normal circumstances, however, acetic acid is to be preferred.

§ 94. Spontaneous coagulation.

When undiluted latex is kept without adding any coagulant, coagulation sets in spontaneously. Sometimes within 24 hours coagulation is already far advanced, but sometimes it takes from 2 to 3 days, and often the serum remains milky.

This spontaneous coagulation was already known in the early days of plantation-rubber; but the putrid smell, that accompanies it, was far from agreeable, and gave rise to the idea (false however, see § 196), that the rubber would be injured by the decomposition processes, so that this method was rejected as wholly unsuitable.

It is only in the modified forms treated in § 95 and 96 that spontaneous coagulation may have some importance in practice. For the study of coagulation, and for the knowledge of these improved processes, the course of ordinary spontaneous coagulation is however of some importance.

For some data on the use of this method in old days, see F. J. HOLLOWAY (*Trop. Agric.* 24 (1904), 160; *J. d' A. T.* 3 (1903), 274 and 5 (1905), 240) who after keeping the latex 24 hours in open pans rolled the coagulum with a wooden pin into biscuits which took 2 months to dry; from the milky serum some 3—5 % of the total rubber was recovered. These data clearly show the disadvantages of this method of coagulation.

See also the general description of the preparation of biscuits in Ceylon, *Bull. Imp. Inst.* 2 (1904), 190.

How the spontaneous coagulation comes about, is not yet completely cleared up. We treated in § 79 the role played by acid-forming bacteria, and the possible action of a coagu-

lating enzyme, supposed by some investigators to be active in producing coagulation.

The degree of acidity, which is obtained in spontaneous coagulation, may reach an amount corresponding with the addition of 2.5 to 3 cc acetic acid per liter of undiluted latex; a much higher dose than with the usual acetic acid coagulation, in which 1 cc acetic acid per liter of undiluted latex is more than sufficient. The explanation of this interesting fact is still undiscovered. The most probable is that in spontaneous coagulation, at the same time as acid-formation, other changes in the non-rubber constituents take place, by which coagulation is retarded.

G. S. WHITBY (VIII Int. Congr. 25, 605; also I. R. J. 45 (1913), 943 and Z. Koll. 12 (1913), 152; see further Agric. Bull. F. M. S. 6 (1918), 377 and 516) found in undiluted latex, spontaneously coagulated, after 6½ hours, an acidity corresponding to an addition of 0.48 cc acetic acid per liter of latex—a quantity much smaller than necessary to produce ordinary coagulation in 6 hours. The same latex, diluted with 5 volumes of water, gave after 24 hours an acidity corresponding with an addition of 3 cc acetic acid per liter of undiluted latex, therefore much more than is used in ordinary coagulation; but coagulation was only very incomplete. This in the first place shows that spontaneous coagulation is not directly related to the amount of acid developed. Further, WHITBY remarks that in the second case nearly twice as much acid is formed as might be expected from the reducing sugars present in latex, so that other substances also must have been attacked and decomposed.

G. VERNET (Bull. Mars. 1 (1919), 117) found spontaneous coagulation to be mediocre when an acidity corresponding to 4–6 gms. acetic acid per liter of serum was produced; but to be good when the amount was 6–9 gms. He found even 10 and 12 gms. after two days, that is much more than other investigators; but perhaps these figures relate to latex to which rather large portions of sugar were added.

VERNET found the maximum of acidity in the serum after two days, and concludes that it is not necessary in spontaneous coagulation to wait longer, with a view to increasing the yield.

The acid formed is for the greater part lactic acid; in addition acetic acid is formed, and some succinic acid.

G. VERNET (Le Latex (1908), 481) mentions acetic acid, lactic acid and butyric acid as the products of fermentation in latex. He further (Bull. Mars 1 (1919), 116) showed that after spontaneous coagulation the sugars have disappeared from the latex (serum), whilst coagulation with acetic acid in the presence of antiseptics such as formalin, or coagulation by heat, leaves the sugars in the serum unchanged.

In spontaneous coagulation a large quantity of gas is formed (principally carbon dioxide); the coagulum therefore becomes spongy and expands. From this type of coagulum, of course, only crepe-rubber can be prepared, and no sheet, which would be wholly filled with gasbubbles.

As was to be expected for a bacterial process, spontaneous coagulation is highly dependent upon temperature. Between 0 and 4° C latex does not coagulate; between 18 and 22° coagulation is very incomplete and slow, and addition of sugar does not give complete coagulation in 24 hours; between 30 and 45° coagulation is perfect. At 50° the fermentation stops, and coagulation by heat begins to show its influence in the latex, if already acid.

See G. VERNET, Bull. Mars 1 (1919), 119.

When the spontaneous coagulation is finished, further changes take place in the coagulum (such as decomposition of proteins) leading to maturation of the rubber and the formation of accelerators. Further, formation of hydrogen sulphide etc. occurs, which changes also take place to some extent in rubber coagulated with acetic acid, and which we will treat in § 107 and 108.

In the air, a yellow slimy layer is formed just as after coagulation with only a small quantity of acid; this will be discussed further in § 107. The formation of this slimy layer must be considered a disadvantage, because, though it is partly removed during washing and milling of the coagulum the remaining part causes streaks and discolouration especially in crepe, while the inner properties of this slimy product are inferior (see § 107). Adding bisulphite to the latex gives no improvement, since this substance tends to retard spontaneous coagulation, and so gives more chance of an incomplete and slow coagulation,

although, under some circumstances, spontaneous coagulation after addition of a small quantity of bisulphite (such as $\frac{1}{2}$ gm. per liter of latex) may be very satisfactory. Putting a layer of water or of a solution of bisulphite on the coagulum, as soon as it becomes sufficiently hard, may sometimes help to prevent the formation of this coloured surface-layer, but it is not always that the coagulation has gone so far in time to do this.

Soaking the coagulum or the fresh crepe in a solution of bisulphite may also help to improve the colour and appearance, but it is not always sufficient.

It is therefore much better to wholly avoid the formation of this yellow slimy layer (the formation of which is in no way necessary and only troublesome) by effecting the spontaneous coagulation in the absence of air, see § 95.

Besides the above named drawbacks, in spontaneous coagulation one has generally to reckon with a loss in rubber, especially in the serum, which seldom becomes entirely clear, and also in milling, as the washing away of the slimy layer causes some rubber to be lost. The decomposition of serum substances may also diminish the final weight of market rubber. Compared with normally prepared crepe, the loss in weight may amount to 1% or more.

See O. DE VRIES and W. SPOON, Arch. 4 (1920), 293 and 308

Rubber obtained by spontaneous coagulation has about the same properties as that coagulated with acetic acid; the tensile strength and slope are the same, the rate of cure is usually greater (10 to 15 minutes in time of cure) and the viscosity also becomes somewhat greater (about 5 units).

G. VERNET, as a result of his early experiments (see Bull. I. Ch. 14 (1911), 805 and 825; Bull. Mars. 1 (1919), 113) mentions that Michelin and Cie found the rubber from spontaneously coagulated latex the best; but in what respect this rubber was superior, is not indicated.

In experiments made by L. E. CAMPBELL in Ceylon (Bull. Ceyl. No. 23 (1915), page 2 and 18; Bull. Imp. Inst. 14 (1916), 501; *ibid.* 16 (1918), 412 and 452) the tensile strength of the spontaneously coagulated rubber was found as good as that of ordinary rubber, whilst the rate of cure was higher (from 14 to 50%).

On the chemical composition of rubber prepared in this manner few data are available.

W. SPOON (Arch. 4 (1920), 284, 290 and 294) found the ash-content the same as in crepe prepared from undiluted latex.

In the experiments of L. E. CAMPBELL (l. c.) the ash-content of rubber from spontaneously coagulated, undiluted latex was found to be higher than in the control, which was prepared from latex diluted 1:1. CAMPBELL'S figures (0.42 against 0.25) are in satisfactory accord with the results of SPOON, taking into account the difference in ash-content between crepe from undiluted latex (compare § 65). The protein-content, though somewhat irregular, was found by CAMPBELL to be usually lower in the samples coagulated spontaneously.

§ 95. Spontaneous coagulation in the absence of air.

The difficulties mentioned in the foregoing paragraph can, for the greater part, be avoided by allowing the spontaneous coagulation to proceed in the absence of air. The yellow surface layer is then not formed, the coagulum remains white, and coagulation is more complete, because the disturbing aerobic processes do not take place.

The latex has to be placed in a closed vessel of some kind, in which enough space is left for the expansion and rise of the coagulum by the gas-formation during coagulation. The vessels used may either be closed hermetically, in which case the gas produced causes a certain pressure; or some kind of water-seal may be used, through which the gases evolved may escape. The simplest—but not wholly satisfactory—form is to cover the coagulating tank with well-fitting boards, or to put a floating cover on the latex, which rises as the coagulum is formed.

A method based on the waterseal-principle has been patented under the name M. C. T. process, see I. R. J. 53 (1917), 495; I. R. W. 58 (1918), 407, and full description and figures in Bull. F. M. S. No. 27 (1918), page 283. See further the discussion by M. BARROWCLIFF (J. S. Ch. I. 37 (1918), 95 T) and W. SPOON (Arch. 3 (1919), 313 and 335).

The acidity developed in the latex is approximately the same as in spontaneous coagulation in the air. After 24

hours the serum shows an acidity of 0.6 normal, corresponding to $3\frac{1}{2}$ gms. acetic acid per liter of serum, or $2\frac{1}{2}$ gms. acetic acid per liter of undiluted latex.

W. SPOON (Arch. 3 (1919), 332 and 337) found the natural acidity of latex, when brought in for coagulation after collection, to be 0.3 normal, which acidity by standing for $3\frac{1}{2}$ hours increased to 0.4 normal.

Besides the acidity of 0.6 normal of the serum, mentioned above, a certain amount of acid is also absorbed by the rubber (coagulum).

In spontaneous coagulation in the absence of air a large quantity of carbon dioxide is developed, and later hydrogen sulphide also. Besides these an inflammable gas (methane?), insoluble in potassium hydroxide, is formed (compare § 107), but this has not yet been investigated.

In this case also the coagulum is spongy and therefore can only be milled to crepe, and, though streaks and discolouration by the yellow surface-layer are avoided, the colour of the crepe still is often somewhat greyish and less satisfactory than that prepared with acetic acid. Bisulphite can be added to the latex only in very small quantities, since it retards the coagulation; soaking the coagulum or fresh crepe in bisulphite-solution however may help, and with sufficient care a good marketable product may be obtained.

Rubber obtained by this method shows a tensile strength and slope equal to that of ordinary crepe, whilst the rate of cure and viscosity are somewhat greater (about 15 min. and 3 units respectively).

The claim that spontaneous coagulation in the absence of air gives a more uniform rubber than ordinary estate-methods is not wholly justified. In so far as only undiluted latex can be used (as diluted latex does not give such a regular and satisfactory coagulation), this process avoids one of the possible causes of variation, viz. dilution of the latex; further it avoids variations caused by different coagulants. But as in standardised estate-preparation both factors are once and for all fixed — a standard dilution, and a fixed amount of acetic acid being chosen — this can

give no advantage over the ordinary estate procedure. Other factors, especially differences in composition of the latex, cause variation in rubber coagulated spontaneously — though to a somewhat lesser degree than in acetic acid coagulated rubber.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 283) made extensive experiments with this process and found the rate of cure generally greater than in acetic acid coagulated sheet or crepe. The figures do not point to a greater uniformity in rubber from latex of different origin and composition, as was supposed by M. BARROWCLIFF (J. S. Ch. I. 37 (1918), 97 T).

W. SPOON (Arch. 3 (1919), 322 and 335; Arch. 4 (1920), 293 and 308) found tensile strength and slope the same as in ordinary coagulation, the viscosity somewhat higher, and the rate of cure some 15% greater, whilst the daily variations were somewhat smaller than when using acetic acid.

The average figures were;

	Tensile strength	Standard time of cure	Slope	Viscosity
Acetic acid coagulation . .	1.38	$118 \pm 4\frac{1}{2}$	36.1	$29\frac{1}{2}$
Spontaneous coagulation in the absence of air . . .	1.39	$106 \pm 2\frac{1}{2}$	35.6	$32\frac{1}{2}$

In special cases however (for instance with latex from trees tapped after a period of rest, or with heavy tapping systems), deviating figures were found, whilst when the coagulum was kept longer than 24 hours before milling, maturation of course proceeded and increased the rate of cure. See also O. DE VRIES and W. SPOON, Arch. 4 (1920), 296 and 308.

The advantage of saving the costs of acetic acid in this process is nullified by the fact that the output in rubber is somewhat smaller, probably because of the decomposition of serum-substances.

Spontaneous coagulation in the absence of air gives on the average 1% less weight than acetic acid coagulation, so that the loss in rubber is greater than the saving in

acetic acid. Hence this process cannot be regarded as economical.

W. SPOON (Arch. 3 (1918), 328) found the decrease in weight to be 0.8% for undiluted latex, and 1.2% when 15% latex was used. See further Arch. 4 (1920), 293 and 308.

Though spontaneous coagulation in the absence of air is a much more satisfactory process than spontaneous coagulation of latex exposed to the air, it has several drawbacks. The principal one is that, in this case also, the coagulation is not always regular and complete; sometimes the latex must be allowed to stand for two days or longer, and this naturally causes a disturbance in the regular routine of work, an accumulation of rubber for milling etc. Especially during and after wintering spontaneous coagulation may be very incomplete, so that measures have to be taken to aid it. What factors retard the coagulation in this way is not yet known, but perhaps a decrease in the content of sugars in the latex may, at least partly, offer an explanation. Also, the process does not take place on all estates with the same ease.

The process can however be regulated in several ways, which fact we will treat in § 96 and 97, viz:

- 1) addition of sugar;
- 2) keeping the latex at a somewhat elevated temperature;
- 3) addition of small amounts of calcium salts, for instance calcium chloride.

§ 96. Coagulation with sugar.

In a cane-growing country like Java sugar is always easily obtainable, and therefore, during the time when acetic acid was scarce, coagulation with sugar attracted a considerable amount of attention.

This method really is a kind of regulation of the spontaneous coagulation: the addition of sugar performs the function of giving food to the micro-organisms and makes circumstances more favourable for the formation of acid.

Coagulation with sugar, and the action of micro-organisms, were first studied by G. VERNET (see Bull. Mars, 1 (1919), 113) whose results however did not become generally known.

It was then taken up again by B. J. EATON (Agric. Bull. F. M. S. 4 (1915), 26; see further *ibid.* 6 (1917), 156 and Bull. F. M. S. No. 27 (1918), 276) who favoured the bacterial theory of natural coagulation and found that sugars promoted this process.

K. GORTER and N. L. SWART (Med. W. J. No. 6, also Agric. Bull. F. M. S. 5 (1916), 48) studied this process in detail and applied it in large-scale experiments on estates. They completely confirmed EATON'S results and studied the bacterial action and the acids formed (see below).

G. S. WHITBY (Agric. Bull. F. M. S. 6 (1918), 513), on the basis of the work of A. I. KENDALL, points to the possibility that the same species of bacterium may produce fermentation (acid from carbohydrates) when carbohydrates are present, but putrefaction (alkaline substances from proteins) when carbohydrates are absent.

DENIER and VERNET (C.R. 165 (1917), 123; see further Bull. Mars 1 (1919), 114) isolated 27 micro-organisms from latex, of which one transformed the sugars in Hevea latex (and also lactose and saccharose) into acid, and was used in special cultures to promote spontaneous coagulation either with or without the addition of sugar.

It is interesting to remark that G. VERNET (Bull. Saigon I (1919), 346; also C. Gp. 1920, 10195) found that large quantities of sugar (as for instance in latex saturated with sugar) prohibited coagulation, as they do ordinary sugar fermentations. Only after 5 days standing a fermentation and gas-formation began in such cases; the latex becoming acidified and completely clotted at the end of 8 days.

To make spontaneous coagulation wholly reliable and regular it is necessary to use at least $1\frac{1}{2}$ gms. and often up to 3 gms. of sugar per liter of undiluted latex, so that the costs (dependent, of course, upon market conditions) are not very different from those of coagulating with acetic acid, and this process—like so many others mentioned in this Chapter—is only resorted to when there is a scarcity of acetic acid.

G. VERNET (Bull. Mars. 1 (1919), 114), on the basis of his above mentioned investigations, recommended the application of this process on a large scale. See also M.E. GIRARD and E. ROSÉ, Public. Gouvern. de l'Indo-Chine, Série Saigon,

No 7, page 45). He holds the sugar-process to be more economical than coagulation with acetic acid. As VERNET (l.c. page 120) prescribes an addition of 1 to 10 gms. of sugar per liter of latex (as necessity may dictate), the larger amounts of sugar would certainly prove too expensive.

K. GORTER and N. L. SWART (l.c.) prescribe a dose of 3 gms of sugar, dissolved in some water, per liter of undiluted latex; but the dose may vary somewhat according to circumstances (composition of latex, possibly its sugar-content, see also § 8).

During coagulating with sugar the serum reaches a degree of acidity of about 0.5 normal, corresponding to 3 gms of acetic acid per liter of serum, and equivalent to the addition of 2 cc of acetic acid per liter of undiluted latex. This is more than is added in ordinary acetic acid coagulation, where 1 gm per liter is more than sufficient. Nevertheless the coagulation is not so fast nor the coagulum so hard, and the serum sometimes remains milky. The explanation of this difference still fails.

See GORTER and SWART, l.c. W. SPOON (Arch. 3 (1919), 333 and 337) found the acidity of the serum after sugar-coagulation to be 0.63 normal, as against 0.53 normal for spontaneous coagulation without sugar.

The acid serum can be used to coagulate latex on the next day; see K. GORTER and N. L. SWART, l.c.; further § 85 and 114.

The acids formed during this process are acetic and chiefly lactic acid, in the proportion of three lactic to one part of acetic acid; besides these, a small quantity of succinic acid is also produced. All these acids have, as far as known, no harmful effect on the properties of the rubber (compare § 92).

See K. GORTER and N. L. SWART, l.c.

The sugar coagulation is accompanied by a large development of carbon dioxide; consequently the coagulum is porous, and inflated like a sponge. It expands during coagulation and rises considerably in the coagulating pans. This gas-formation makes it impossible to mill the coagulum into anything but crepe. If one desired to make sheet rubber, he would have to ferment the sugar separately first,

either in water or in serum, and with the acid liquid so obtained produce coagulation (see § 93).

A drawback of this process is that in contact with the air a slimy yellow layer develops, as in other slow coagulation processes. To prevent discolouration and streaks in the crepe one has to keep the coagulum free from contact with the air. Even then the colour of the crepe is often rather dark and irregular. Bisulphite can be used in small quantities which then noticeably improve the colour, but it delays the action of the bacteria and sometimes retards the coagulation too much. Another expedient, by which the colour is much improved, is the soaking of the coagulum or the freshly milled crepe in a bisulphite-solution.

See for instance B. J. EATON, J. GRANTHAM and F. W. F. DAY, Bull. F. M. S. No. 27 (1918), 369.

Coagulation with sugar produces a crepe which in inner properties is practically identical with crepe prepared with acetic acid. Small differences may appear, dependent upon the circumstances. The uniformity of the product from day to day may be quite the same as in ordinary preparation.

See O. DE VRIES, Arch. 1 (1917), 5. In a large number of experiments with sugar coagulation the tensile strength was found to be exactly the same as when acetic acid was used. The rate of cure was sometimes somewhat larger, at other times somewhat smaller, according to circumstances, but the daily variations were not greater than those with acetic acid. The slope was the same, and the viscosity showed only small deviations from the control samples.

A. J. ULTÉE (Arch. 2 (1918), 339) found the viscosity for crepe prepared with sugar to be lower than that of the acetic acid control; K. GORTER and N. L. SWART (Med. W.J. No 6, page 14), however, in large scale experiments found that the viscosity was not affected by sugar-coagulation.

G. VERNET (Bull. Mars. 1 (1919), 113) mentions that from tests by the Maison Michelin & Cie it appeared that addition of sugar to the latex did not in the least injure the properties of the rubber.

No difference in weight, as compared with crepe prepared in the ordinary way, could be detected.

W. SPOON (Arch. 3 (1919) 329 and 337; *ibid.* 4 (1920), 293 and 308) found no difference in weight of crepe when coagulating undiluted latex either with acetic acid, or with sugar (2 gms. per liter of latex) and then rolling the coagulum the following day.

§ 97. Other ways of furthering spontaneous coagulation.

Spontaneous coagulation, preferably in the absence of air, can be furthered in several ways, other than by the addition of sugar.

1) Keeping the latex at an elevated temperature.

The bacterial processes, by which acid is formed and which cause spontaneous coagulation, proceed more quickly and better at a slightly higher temperature than the ordinary room-temperature in the tropics (which is 27—30° C). A temperature of 40° C seems to be the most favourable, and by keeping the latex in a warm spot, or by heating small quantities of latex in an incubator, a more perfect spontaneous coagulation can be obtained.

M. BARROWCLIFF (J. S. Ch. I. 37 (1918), 50 T) roughly estimated the optimum temperature to be 55—60° C, but this seems to be rather too high.

G. VERNET (Bull. Mars. 1 (1919), 119; Bull. Saigon 1 (1919), 343) found a temperature between 30 and 45° C the most favourable, and W. SPOON (Arch. 3 (1919), 319 and 336) found 50° too high, 40° C very favourable, whilst the heating needed not to be prolonged more than 8 hours.

The properties of the rubber, the weight obtained, and the difficulties with the surface (somewhat darker colour) are exactly the same as in spontaneous coagulation without heating.

See W. SPOON, *l.c.*

2) Addition of small amounts of calcium chloride.

The addition of small amounts of calcium chloride, such as $\frac{1}{2}$ gm. anhydrous chloride (or $\frac{1}{4}$ gm. calcium) per liter of latex, may greatly further spontaneous coagulation,

which becomes more rapid and complete, and is even satisfactory in cases where spontaneous coagulation does not succeed well without this addition.

The explanation of this phenomenon is not yet clear. It was advanced by some as a proof that enzymes play a role and are activated by this substance, but the simple action as a salt may also offer an explanation.

See L. E. CAMBELL, J. S. Ch. I. 36 (1917), 274; M. BARROWCLIFF J. S. Ch. I. 37 (1918), 50 T.

The properties of the rubber, the weight of the crepe and the outer appearance of the product are exactly the same as in the foregoing cases, whilst the ash-content of the rubber shows a small increase only when rather large doses (such as 1 gm. of calcium chloride per liter of latex) are used.

W. SPOON, Arch. 4 (1920), 273 and 289.

§ 98. Smoke and smoke-constituents.

In order to imitate the real or supposed advantages of the Brazilian method, a number of processes have been projected, and many of them patented, in which latex is coagulated by means of smoke, often by cleverly planned apparatus. Except for the Brazilian method itself, of which we shall speak in Chapter XIV, none of these methods, so far as we know, has established itself in actual practice. This is because the expected improvement in the qualities of the rubber was not obtained; further because these methods, when a regular and complete coagulation is desired, generally require more care and supervision than the ordinary process of preparation.

Relatively little is known of the way in which coagulation takes place in these methods. In most of them heating plays a role, furthermore the acid constituents of the smoke play a part, among them acetic and formic acids. By some authors a great significance is attributed to carbonic acid, and others consider the formaldehyde, creosote and tarry constituents of the smoke very important factors.

R. H. BIFFEN (Ann. Bot. 12 (1898), 166) was one of the first to draw attention to the action of the smoke in the Brazilian method of coagulation, and especially to the acetic acid contained in it, besides the evaporating action of the heat.

That strongly deviating qualities may be secured in coagulation by heating will be shown in § 99, while in § 146 the decrease in rate of cure by the action of smoke-constituents is discussed. If one further considers that in some of these processes the rubber is worked into thick slabs and dried slowly, so that maturation may take place, there are evidently causes enough which may effect changes in the inner qualities, and which will have to be investigated and explained separately for each case.

For only a few of these processes are there sufficient investigations and data available.

The *Derry process* is described by its inventor in the Gard. Bull. 1 (1912), 81, see also I.R.J. 44 (1912), 50 and 49 (1915), 631. Experiments with it by B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 256) showed this process to give a rate of cure somewhat faster than Fine Hard Para, but there was nothing to recommend this process, which is rather complicated and requires much care and supervision.

The apparatus invented by R. W. LASH is described in Rubb. Rec. 1914, page 380.

About the *Byrne process* see B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 267), who did not find any advantage in the use of this method.

In the experiments of L. E. CAMPBELL (Bull. Imp. Inst. 14 (1916), 539) Byrne cured rubber was found to vulcanise slowly, apparently because of the content of smoke-constituents, but a sample of Byrne loaf, a rectangular cake pressed when still moist, cured rather rapidly.

The *Wickham process*, giving a wet rubber which looses about 10% on washing, was found also to produce a rather rapid curing rubber (Bull. Imp. Inst. 14 (1916), 539).

One can also get a coagulating fluid by catching smoke constituents in water. The liquid so obtained of course need not contain tarry constituents and in this respect has an advantage over the acid fluid obtained by distillation of wood (see § 84). The yield in acetic acid is much smaller in this procedure, but on the other hand no wood is needed for heating the furnace, as in distillation.

For relative costs and yields of these processes, and their further application, see B. J. EATON and G. S. WHITBY, *Agric. Bull.* 5 (1917), 124 and further B. J. EATON, J. GRANTHAM and F. W. F. DAY, *Bull. F. M. S.* No. 27 (1918), 247. By slow combustion of Hevea wood a liquid containing $1\frac{1}{2}$ to $2\frac{1}{2}\%$ acid was obtained, but this liquid contained a good deal of tar, which could be removed by filtration. The rate of cure of the rubber was found to be somewhat retarded by the use of this „smoke solution” as a coagulant.

§ 99. Alcohol and denatured spirit.

Alcohol is one the oldest coagulating media, and has been used by preference by many investigators because it gives a quick coagulation and, provided that sufficient is used, it need not be dosed exactly. Therefore it is a quick and a simple medium for trial coagulation.

In practice it is not useful as a coagulant. In the first place it is too expensive, even when alcohol in the form of denatured spirit is used, because for the complete coagulation of 1 liter of undiluted latex at least 250 cc of denatured alcohol is necessary, which would mean some 10 times the cost of acetic acid.

In the second place the type of coagulation by alcohol is wholly different from that by acids. Alcohol gives an immediate clotting; in the place where the alcohol is poured into the latex a clump of coagulum is formed even if one stirs rapidly. This clump encloses relatively a large part of the alcohol, which diffuses out of it only little by little.

With alcohol the coagulation is therefore sudden, while with acids it is gradual. If one desires to obtain directly a complete coagulation by alcohol by stirring thoroughly, it is necessary to add even 500—600 cc of denatured alcohol per liter of undiluted latex. If only 250 cc is added (see above), then the serum remains white and the coagulation only becomes complete by the diffusion of the alcohol out of the already formed clot. On the following day one has a clear serum, but sometimes not all of the rubber gathers on the lump and portions of it drift as loose flocks in the serum.

In § 75 we have already referred to the investigations of V. HENRI (C. Gp. 1906, 512), who studied coagulation with alcohol in dialysed latex. Dialysed latex itself is not coagulable with alcohol. After addition of salts of monovalent metals alcohol gives an agglutination, but only when the salts are added in a concentration of approximately 10%. Salts of bivalent metals have a much stronger effect, even $\frac{1}{100}$ normal giving coagulation, whilst when the amount of alcohol or the amount of salts is decreased, the effect is only agglutination. The addition of very small amounts of alkali (for instance $\frac{1}{10,000}$ normal of sodium hydroxide) prohibits agglutination or changes a coagulation into an agglutination. These facts are well fitted to illustrate the influence of accessory substances on coagulation.

The wholly different action of alcohol makes it necessary to use only a strong alcohol (for instance 95% and higher), while the latex must always be undiluted. Diluted latex contains too much water, and abnormally large quantities of alcohol would be necessary to obtain coagulation in it.

The rubber coagulated with alcohol, being in the form of an irregular clot, can of course be milled only into crepe. The rubber is pale in colour; the crepe dries rather slowly, the drying time being perhaps $\frac{1}{4}$ longer than for ordinary crepe.

On the other hand it is an advantage that an excess of coagulant does not hinder, as is the case with acetic acid and other acids, but rather promotes a rapid coagulation and clearing of the serum. If only a sufficient quantity is added, alcohol need not to be measured or dosed, but always gives a satisfactory coagulation; and this, as we mentioned above, makes it a very handy medium for trial coagulation or in experiments where the only aim is to get all the rubber out of a certain latex rapidly and easily (for instance in determinations of production of individual trees, and so on).

See O. DE VRIES, Arch. 4 (1920), 199 and 217.

Whilst the use of alcohol in practice is very limited, this coagulation may present a certain scientific interest, because it is of so wholly different a type and course.

It is remarkable that the inner properties of the rubber are nearly the same as after coagulation with acetic acid; tensile strength and rate of cure showing no difference, but slope and viscosity deteriorating somewhat.

Compared with crepe from undiluted latex, coagulated with acetic acid, the slope may increase by 2—3 units, and the viscosity decrease by 0—7 units. Different kinds of denatured spirits gave the same results.

See O. de VRIES, H. J. HELLENDORRN and W. SPOON, Arch. 4 (1920), 202 and 217.

This combination—change in slope and viscosity, whilst tensile strength and rate of cure remain the same—is uncommon and therefore interesting; an explanation however is still wanting.

See also Bull. Imp. Inst. 16 (1918), 452, where in one sample, coagulated with alcohol, the properties after vulcanisation were found to be exactly the same as in the control, whilst the chemical composition showed no marked difference and the protein-content was even found somewhat lower.

Perhaps one would expect alcohol to precipitate proteins and other substances from the serum at the same time as the rubber with its customary constituents. This has not been investigated fully, but in § 111 we will see that after coagulation with alcohol the alcoholic serum still contains proteins precipitable by heat to the amount of $\frac{1}{4}\%$ (calc. on the original serum), whilst serum after acetic acid coagulation contains $\frac{1}{6}\%$. The difference in precipitating effect and in composition of the rubber seems to be less than one would expect. This is corroborated by the fact that alcohol-coagulation in undiluted latex gives not quite 0.5% more in weight than acetic acid coagulation, so that certainly the rubber does not retain much more serum substances.

O. DE VRIES, H. J. HELLENDORRN and W. SPOON (Arch. 4 (1920), 204 and 218) found an increase in weight up to 0.7%, in the average 0.44%, by coagulation with alcohol, as compared with acetic acid crepe from undiluted latex.

The ash-content was found to be decidedly higher, being some 0.40% of the crepe, against 0.24 in the controls.

The fermentation of alcohol, by which a dilute acetic acid may be obtained, gives much more economical results, as was shown in § 84.

§ 100. Coagulation by heat.

Coagulation can also be brought about by heating the latex. At from 60° to 70° C the undiluted latex usually begins to thicken and at about 80° (dependent upon various conditions, such as rubber-content and degree of acidity of the latex) coagulation takes place. Generally the serum remains quite white; sometimes by further heating or by boiling most of the rubber may be obtained, but sometimes (namely if the white serum contains only a little rubber) this does not succeed, and it is often difficult to get this small amount of rubber coagulated, even by the aid of acetic acid.

The temperature, at which coagulation (or better flocculation) takes place, is markedly diminished by adding small amounts of acid to the latex. The influence of the natural acidity of latex on the temperature at which coagulation takes place has not yet been studied in details, but the temperature at which the latex coagulates diminishes with the development of natural acidity on standing.

See G. VERNET, *Bull. I. Ch.* 14 (1911), 808. Further G. S. WHITBY (*VIII Int. Congr.* 25, 609; also *I. R. J.* 45 (1913), 943 and *Z. Koll.* 12 (1913), 153; further *Agric. Bull. F. M. S.* 6 (1918), 379). Even by treating the latex with CO₂ a reduction of about 8° in curdling temperature of the latex could be obtained.

Dilution of the latex greatly hinders coagulation by heat, and a sufficiently dilute latex (for instance 1:1), when fresh, will not coagulate even on boiling, but remains perfectly stable.

See J. PARKIN, *Circ. R. B. G.* 1 (1899), 145. Further G. S. WHITBY, *l.c.*; M. BARROWCLIFF, *J. S. Ch. I.* 37 (1918), 49 T.

In practice this method is somewhat too complicated, and the loss of rubber due to the often incomplete coagulation is a further drawback. Heating has however been used to separate remnants of rubber from milky serum, washings

and such dilute fluids, after adding some acid if necessary. The product so obtained is mostly very inferior.

The effect of coagulation by heat is interesting in relation to other processes, in which heat is applied, such as the Brazilian method (see Chapter XIV). Besides, heating the latex (though not until complete coagulation occurs), in former years, found application on many estates, as a means of obtaining a pale rubber free from oxydation. Heating the latex destroys the oxydising enzyme (see § 12, 47 and 51), but is now completely replaced by the much better and easier method of using bisulphite (§ 48).

Passing steam into the latex until the temperature reaches 80° C, which temperature had to be maintained for 15 minutes or longer, was recommended by M. KELWAY BAMBER as a method of avoiding discolouration due to oxydation (see Lectures 1908, page 73; Agric. Bull. Str. F. M. S. 7 (1908), 347, and Trop. Agric. 31 (1908), 300).

Defecation, that is heating the latex till a precipitate or a kind of pre-coagulation rises to the surface, was used in former years as a means of purifying the latex. Coloured matter, dirt etc. are enclosed in the first formed clots, and the remainder of the latex gives a very pure white rubber. See A. J. ULTÉE, Rubb. Rec. 1914, page 391, and also § 176.

Coagulation by heating the latex (without addition of acid) produces a rubber which vulcanises quickly, in about half of the usual time for crepe. The tensile strength does not decrease with this method of coagulation, or at most to a very slight degree; the slope remains unaltered, the viscosity however becomes markedly smaller.

The following figures may serve as an example.

	Tensile strength	Standard time of cure	Slope	Viscosity
Coagulated by heating the latex	1.40	135	36½	24
Control, coagulated by acetic acid	1.36	75	36½	19

See O. DE VRIES and H. J. HELLENDORRN, Arch. 2 (1918), 540 and 557.

Here again we have an example of a method of preparation which gives a greater rate of cure with a smaller viscosity. It is not known by what change or by what component the greater rate of cure is caused. The decrease in viscosity is probably due to the simple physical effect of heating.

The data concerning the chemical composition of rubber coagulated by heating are also still very incomplete. The ash-content is higher than that of normal crepe.

The effect of heating latex, to which acid has been added, is somewhat different; in so far as heating puts a stop to all maturation, it may even retard the rate of cure.

In experiments by L. E. CAMPBELL (Bull. Ceyl. No. 23 (1915), page 13; Bull. Imp. Inst. 14 (1916), 503), in which acetic acid was added to the heated latex, the tensile strength was found not to be affected. The rate of cure was however the same or even smaller than in the ordinarily prepared control-crepe or sheet; the chemical composition was unchanged.

For some data on latex coagulated with acetic acid, into which steam was passed after addition of the acid, see S. MORGAN (Prep. Pl. Rubber, page 93), who found the colour of the crepe somewhat paler, but the drying much slower, and the properties (resiliency, recovery and resistance to stretching) less satisfactory.

§ 101. Coagulation by cold.

Latex cooled to a temperature somewhat above 0° may be preserved for a long time, and this cooling of latex may even be of help in its transportation over long distances.

G. VERNET (Bull. Mars 1 (1919), 115) kept latex perfectly fluid for over a month by keeping it at a temperature never higher than 4°C, and mentions the regular transport of latex to the laboratory over a distance of 70 kilometers by the aid of cold. See also J. BOUTARIC, C. Gp. 1911, 4963.

When frozen, the diluted latex may be melted again to practically the same condition as before; but when kept frozen for several hours (preferably, of course, undiluted

latex), coagulation takes place. The rubber so obtained has the same tensile strength and rate of cure as when coagulated with acetic acid; maturation however does not take place at low temperatures (compare § 108).

J. PARKIN (Circ. R. B. G. 1 (1899), 145) stated that dilute latex, when frozen to a solid block, melted to practically its previous condition and showed no signs of separation.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. 27 (1918), 264, see also J. S. Ch. I. 35 (1916), 722) found that latex can be frozen for a short time and on thawing be reconverted into latex; but when frozen 4—8 hours, a solid coagulum is formed.

E. FICKENDEY (Z. Koll. 8 (1911), 45) recommended freezing as a means of obtaining the serum (of *Funtumia* latex) in the original state (without coagulant). This method deserves attention.

§ 102. Coagulation by evaporation.

Latex may be completely dried up by simple evaporation in the air. This occurs in practice, when during dry weather a thin solid film forms on the surface of the latex in the cups, or when films of the latex dry on the walls of the cups in the form of cup-film after the latex is collected (see § 180). Larger quantities of latex, however, can only be brought to dryness by exposing them in a very thin film to a current of air. In practice this method has been worked out in the Kerbosch-process, under application of heat, as will be treated in § 193.

The process of coagulation during evaporation has not yet been studied in detail. Some flocking may be observed in the films as the mass gets drier, but on the whole a simple solidifying seems to take place, without separation into coagulum and serum.

Thin films of latex, dried by rapid evaporation in the air, or rubber prepared after the Kerbosch-process, contain all the solids from latex; the total weight so obtained is 10 to 12% larger than when crepe is prepared according to ordinary methods. The rubber contains water-soluble substances, it is hygroscopic to some degree, and very liable to mouldiness, which fault may be corrected by soaking the films in water.

Extraction with water does not remove all the substances that remain in the serum in ordinary acid-coagulation; the watery extract is only $4\frac{1}{2}\%$ of the rubber, whilst ordinary serum contains 5% of solids, which means 3.3% calculated on the latex or 10% on the rubber (corresponding with the increase in weight, see above), so that not quite half of the extra substances is extracted by boiling with water.

These figures hold for thin films of latex dried rapidly in the air.

The watery extract from different rubbers prepared by evaporation was found by the Government Institute (Comm. Delft II, 66) to be from 4 to 6.5% .

About the composition of the watery extract, that is the substances which are most easily dissolved from the rubber, nothing is as yet known.

Comm. Delft II, 55.

When the films are fresh a proportion of the proteins may be extracted, which are still water-soluble in the fresh thin films, but which are rendered insoluble by acid coagulation.

G. VERNET (Bull. Mars. 1 (1919), 112; Bull. Saigon I (1919), 344) indicated this method as a means of obtaining a solution of the proteins from latex. The extracted rubber contained only $\frac{1}{3}$ of the amount of nitrogen present in ordinarily prepared crepe.

The loss on washing of films of rubber dried up in the air is generally the same as the loss on extraction with water (compare § 193).

The dried up latex, of course, has a composition other than that of ordinary crepe or sheet; the following are typical figures for unwashed films, which, however, may vary according to circumstances:

Moisture	3 %
Nitrogen	0.5 %
Ash	1.5—2 %
Acetone-extract	3 %

The nitrogen-content is therefore approximately twice as great as in ordinary rubber; but presumably a great part is not present in the form of protein.

The ash is some six times as great as in ordinary rubber, in accordance with the figures in the table on page 14.

Quebrachite and sugars may also be expected to be present in the dried up latex; but to determine their amount from the watery extract by the polariscope is difficult, because of the dark colour of this extract.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 112) mention a nitrogen content of 0.5% for rubber from evaporated latex—an example of a rapid curing rubber with a high nitrogen content.

P. DEKKER (Comm. Delft II, 67) for three samples of trade-rubber obtained by evaporation of the latex, mentions an ash-content of 1.43 to 1.83, nitrogen 0.70—0.86, acetone-extract 3.3—3.6, water extract 5.58—6.93. The rubber, after extraction with water, still contained 0.50 to 0.85% ash (appr. $\frac{1}{3}$ of the total ash) and 0.53 to 0.57% nitrogen.

The rubber obtained in this manner shows a normal tensile strength, slope and viscosity, whilst the rate of cure is approximately the same as that of unsmoked sheet, and somewhat greater than that of ordinary crepe or smoked sheet (time of cure 70—80 minutes against 100—120 minutes for ordinary rubber).

B. J. EATON and J. GRANTHAM (J. S. Ch. I. 35 (1916), 724; Bull. F. M. S. No. 27, 78) found films of latex rapidly dried up in the sun or by smoke to cure quickly, the rate of cure being 110—155% of that of smoked sheet. Several samples, due to causes not explained, even cured as quick as matured rubber.

It is interesting to remark that washing and crepeing does not or only little change the properties of this rubber, the time of cure increasing only by 5 minutes or less. The substances causing the increased rate of cure are evidently not easily removed by crepeing.

When the latex is dried till a solid mass is formed without driving out all the moisture, the wet coagulum may, of course, mature and become more rapid in cure; the time

of cure may decrease to 50—60 minutes, with the accompanying increase in viscosity.

Analysis of a very rapidly curing sample prepared by evaporating in a vacuum drier and evidently matured see Bull. Imp. Inst. 14 (1916), 550; *ibid.* 16 (1918), 439.

§ 103. Coagulation by mechanical means.

In contrast to other latices, Hevea latex does not yield its rubber readily on mechanical treatment.

Centrifugation does not lead to separation of the rubber globules, though the difference in specific gravity between the rubber and serum may be regarded as large enough (see § 15); and it is only when a small amount of acid is added, that the incipient coagulation may be helped by centrifugation. This however is of no practical importance, as the same separation is reached when the acidified latex is kept for some time.

The statement of R. H. BIFFEN (*Ann. Bot.* 12 (1898), 168) that Hevea-latex may be centrifuged in the same way as *Castilloa*, could not be confirmed by J. PARKIN (*Circ. R. B. G. I.* (1899), 143; *I. R. J.* 36 (1908), 458, *Trop. Agric.* 35 (1910), 6, also *I. R. J.* 39 (1910), 652), nor by K. BAMBER (*Trop. Agric.* 25 (1905) *Suppl.*, page 11; *Circ. R. B. G.* 3 (1906), 297) and H. WRIGHT (*Trop. Life* 3 (1907), 69), who tried, but without success, to obtain a separation by increasing the density of the mother liquid by adding sodium sulphate.

H. S. SMITH (*Lectures* 1908, 231) obtained a separation in Hevea-latex by centrifuging after addition of acetic acid. See discussion *ibid.* page 202, and description of apparatus *J. d'A. T.* 11 (1911), 382.

CL. BEADLE and H. P. STEVENS (*VIII Int. Congr.* 9, 22; also *Z. Koll.* 13 (1913), 210) found that no separation took place unless aggregates had already formed.

G. VERNET (*Bull. Mars.* 1 (1919), 113), also mentions that centrifugation at 6000 revolutions per minute during a period of half an hour did not lead to coagulation. Only a thin film of gum separated, which it was difficult to remove from the milky liquid.

In the same way, *churning* Hevea-latex does not lead to complete coagulation. A clot may be formed, just as by

slow stirring, or a partial coagulation may be obtained (see § 176). Continued churning may give further separation of rubber, but does not seem to give complete coagulation, unless the latex is kept so long that spontaneous coagulation takes place. The mechanical treatment may probably help the formation of clots or lumps by natural (still little known) causes, or perhaps further the thickening and formation of films by evaporation. But it is evident that processes which necessitate special mechanical treatment have no practical significance, unless they give a good, complete coagulation in a much shorter time than when spontaneous coagulation without any treatment is allowed to take place.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 37; also Z. Koll. 13 (1913), 218) found churning or shaking without coagulating effect, as well on normal latex on plantations, as when using dialysed preserved latex.

Churning after the addition of sufficient amounts of acid may however lead to a rapid separation of the rubber, and this principle, worked out under the name of Michie-Golledge process, was for a long time in use on many estates.

In the same way, vigorous churning or stirring of the latex to which a rather large dose of acetic acid has been added, for instance for trial coagulation, may greatly further the rapid formation of a coherent clot and unite the particles of the first formed mass, which on simple standing remains weak for some time.

Whether shaking the latex, either with air or in a nearly filled vessel, has a clotting influence, is not yet sufficiently investigated. This point, of course, is of interest for the formation of lump during transport to the factory (see § 38 and 177); but the question is complicated by the natural acidity of latex and other factors, which are not yet sufficiently cleared up.

The above described behaviour of Hevea-latex, different from other latices, is generally ascribed to the smallness of its rubber-globules (see § 1 and 18).

§ 104. Coagulation with papain.

It is of interest to mention that latex may be coagulated by the addition of papain in the crude state (dried sap from the fruits of *Carica Papaya*). On addition of a 1 % solution of this powder per liter of latex coagulation proceeds as with double the amount of 1 % acetic acid; and when using more papain-solution, coagulation may be very rapid and complete.

More interesting still is the fact that coagulation also follows when the latex is made and kept alkaline, neutralising the acids formed by the decomposition of the proteins by the enzyme.

The decomposition of proteins by papain is well known; this method of coagulation deserves further systematic study, to see in how far coagulation runs parallel with decomposition of the proteins.

A. J. ULTÉE, *Teysm.* 28 (1917), 179. The nitrogen-content of crepe prepared with papain was 0.25 %, against 0.35 % for the control coagulated with acetic acid. Tensile strength and rate of cure were normal; the viscosity was very high (see *Arch.* 2 (1918), 343). The rubber however dried extremely slowly, and it was not possible to get sheets, prepared with papain, completely dry in an ordinary estate smokehouse.

In experiments made in Ceylon (*Bull. Imp. Inst.* 16 (1918), 451), 1 part of papain, mixed with water, was added to 320 parts of latex, which immediately started clotting. The crepes vulcanised rapidly (rate of cure 117 — 158 % of normal) and showed a high ash-content (0.4 — 0.6 against 0.33); the nitrogen-content however was normal or even somewhat higher, the resin-content was high.

The experiments of H. C. T. GARDNER (*Lectures* 1908, 227) and D. SPENCE were treated in § 77.

CHAPTER VII.

THE COAGULUM.

§ 105. The structure of the coagulum.

Coagulation, as we saw in Chapter V, may proceed in very different ways, according to conditions. Sometimes the latex congeals slowly and, as it were, without noticeable transition into a solid cake; sometimes a clotty fluid is first formed, or a sort of porridge-like mass, which slowly coheres; sometimes also one sees first a separation of fine floccules taking place.

We treated these different forms of coagulation in Chapter V. The end, with Hevea-latex, is always the formation of one coherent mass, but on the properties and consistency of this mass the way in which it is formed may, of course, be of large influence. The less the coagulum is worked, the more readily such differences are distinguishable in the finished rubber. Biscuits, Brazilian balls and such forms still show the consistency of the original coagulum to some degree, whilst in crepe-rubber much has been changed by the milling.

The structure of the coagulum was especially studied and described by V. HENRI (C. R. 144 (1907), 432; *Le Latex*, page 349; C. Gp. 1907, 1066) who gave micro-photograms for different types of coagula and laid stress on the following points:

- 1) The structure of the coagulum varies with the nature and concentration of the coagulant.
- 2) A weak coagulant produces the formation of a powdery or flocky precipitate; a strong coagulant gives on the contrary an elastic clot with reticular structure.
- 3) The elastic properties of the rubber obtained by coagulation from the same latex vary considerably with the coagulant used.

The differences observed by HENRI however relate to dialysed latex, and to very different coagulants. His conclusion, as

to the importance of the structure of the coagulum in connection with the properties of the rubber, seems exaggerated for ordinary plantation-rubber, in which the structure of the coagulum — because of the small number of coagulants that are actually used, and also because of the coagulating influence of the soluble serum-constituents — shows much smaller variations.

Whether the rubber-globules during coagulation wholly coalesce to form one homogeneous structureless mass, or whether they only stick together, keeping their original globular form, is still a subject of debate.

See, for instance, PH. SCHIDROWITZ (J. S. Ch. I. 28 (1909), 6; I. R. J. 37 (1909), 98, and Rubb. Rec. 1914, 368), who distinguished globules, apparently the unchanged rubber-globules from latex, in dry Hevea and Funtumia rubber, but whose observations could not be confirmed by E. FICKENDEY (Z. Koll. 8 (1911), 46).

On the fusion of globules to larger ones in latex of Ficus and Castilloa, see CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 20; also Z. Koll. 13 (1913), 209). These authors found the fusion in Hevea-coagulum far less complete, a fact which they ascribe to the higher protein-content (l.c. page 30 resp. 214).

Certain irregularities, which convey the impression of a net-structure, can be made visible in coagulum or dry rubber by different dyeing methods. The real significance of these structural discontinuities is, on account of the delicate and delusive nature of such dyeing methods, not easy to determine, and it may not yet be regarded as definitely settled whether they constitute a real network of protein or other fibres, or whether they are only caused by local differences in physical condition, or some other cause.

D. SPENCE (Lectures 1908, 195 and I. R. J. 35 (1908), 24 and 93) investigated Para-rubber, which has the advantage of not having been worked after coagulation. By staining with a silver nitrate solution and reducing with tannic acid made alkaline by a sodium carbonate solution, a fine meshwork was made visible (see illustrations l. c.), which SPENCE ascribed to proteins. He holds this protein-network to be very important for the tensile strength of the caoutchouc-mass.

PH. SCHIDROWITZ (Rubber, page 127) gives illustrations showing reticular structures in Funtumia-coagulum.

H. C. T. GARDNER (Rubb. Ind. 1911, 227) holds a protein-network to have nothing to do with the formation of a coherent clot, as the caoutchouc still can be obtained in a tenacious mass after digesting the latex with papain at 50° C for 24 to 36 hours and dialysing the converted albumins which are then soluble. No nitrogen or other determinations are given, however, to show that the proteins were wholly removed.

On a network in rubber, and on the conception of rubber as an emulsion or colloidal solution with two phases, which can be distinguished by treating it with solvents, see A. TSCHIRCH, G. Ztg. 33 (1919), 930 and D. F. TWISS, Annual Report Soc. Chem. Ind. 4 (1919), 321.

The consistency of the coagulum, or better still that of the dry rubber, is generally tested by hand-pulling, tooth or nail tests. All such tests are very uncertain, as we will see in § 230.

As, however, hand tests are easy and vulcanisation- or other tests are long, wearying and troublesome, great importance is still being attached to hand tests, especially by those who never control their judgment by accurate vulcanisation and other researches. Consequently a perhaps somewhat exaggerated importance is often given to the structure, consistency and properties of the coagulum.

As to the importance of the properties of the coagulum and the way it is formed, it seems desirable to clearly distinguish two points, viz. the properties of the raw rubber, and the properties of the vulcanised product.

That the properties of the raw rubber may to a large extent be influenced by the way in which the coagulum is formed, follows from phenomena so general in colloidal chemistry, that it needs no further proof or corroboration for rubber. In fact, it is well known that every stage in the life-history of a colloid has an influence on its final properties.

As properties falling under this head may be named the toughness and elasticity of the raw rubber, its strength and stress in hand-pulling, the plasticity of the rubber, its milling capacities, the velocity and ease with which it breaks down on the rolls, swells in solvents, or goes into solution. All these properties are of importance in manu-

facturing practice, as they determine the ease and regularity with which the raw material can be worked, and, in case it is used in the unvulcanised form, also determine its final properties to a certain degree.

It might be that in cold vulcanisation, a much less drastic process than vulcanisation by heat, the structure of the raw rubber is to some degree retained. It would be interesting to investigate whether in this direction the explanation may perhaps be sought of the real or supposed superiority of Brazilian rubber in making elastic thread etc.

These properties should be carefully distinguished from the properties of the rubber after vulcanisation. Vulcanisation is such a drastic process, the influence of a prolonged heating to 130—150° C is unavoidably so great, and the resulting sulphuretted product is so different from the raw material, that the vulcanisation-process may be regarded as a total reconstruction of the colloidal mass, by which process it is broken down into its elements and rebuilt step by step, completely losing its original structure and what may be called its superficial properties. Even when viscosity is determined as in our tests (see § 232—237), where the rubber is dissolved in benzene to a 1% solution, most of the structural peculiarities of the coagulum, which are apparent to the hand and eye, lose their significance and are destroyed in this destructive process of solution.

See also CL. BEADLE and H. P. STEVENS (I. R. J. 35 (1908), 26), who argue that the reticular structure must be lost during vulcanisation, the rubber being brought into a semi-liquid state.

A few examples may serve to clear up this point.

Coagulation with alum, especially when more is used than is strictly necessary, gives a rapid formation of a coherent clot, which soon becomes very hard and tough, and when rolled into sheet is very resistant to stretching and which, with the hand-pulling test, appears strong and elastic. It is as if the astringent properties of alum make themselves felt to a certain extent. When, however, the viscosity of such a rubber is determined it is found to be low, evidently because it is decreased by the traces of coagulant absorbed in the rubber; on vulcanisation, the rubber is found to cure very slowly and the strength of the vulcanised

product may be inferior, being decreased either by the long heating that is necessary for so slow-curing a product, or by the traces of the coagulant left. Thus, an apparently very strong coagulum (sheet) may show inferior qualities in testing.

On the other hand, a certain brittleness or shortness is sometimes noted in sheet-rubber, which on hand-pulling easily snaps; the viscosity of such rubber is generally somewhat inferior, but the properties after vulcanisation, and especially the tensile strength, may be quite normal, so that the deficiency in strength of the raw rubber wholly disappears in the reconstruction of the material during vulcanisation.

Further, when sheet-rubber is prepared from very dilute latex (say 10 % rubber or less), a weak and flabby coagulum is obtained, which during milling perhaps does not harden sufficiently, and when hung to dry may stretch considerably. The rather thin sheet obtained from it may give an impression of weakness on hand-pulling, but after vulcanisation quite a normal product is obtained (see § 64). In this case again, the varying and somewhat weak structure of the coagulum, especially while it was still wet, wholly disappears during vulcanisation.

The opinion is often heard that the rubber is stronger when the coagulum is formed undisturbedly; this is in close relation to the conception that raw rubber has something of a fibrous structure. When, however, the mass is constantly stirred during coagulation, so that a clotty porridge-like mass is formed, which gradually sticks together, and in which every kind of long fiber would have been destroyed, the viscosity and properties after vulcanisation are exactly the same as in rubber from a wholly undisturbed coagulum.

See also CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 9, 29; also Z. Koll. 13 (1913), 214) who found no difference in quality of the rubber that could be traced to the structure of the coagulum, when either a firm coagulum was formed by rapid and complete coagulation, or a loose collection of flocculent aggregates (small clots) by very slow coagulation, which could only be united by filtering or by pressure between cloth.

The same, to a certain degree, is the case with the much stronger disturbance of the structure by crepeing. As we will see in § 118, the mechanical action itself, the tearing and kneading, is absolutely without influence on the properties after vulcanisation; and the cohesiveness of the young, fresh coagulum is so great that it stands this tearing with ease and, in spite of it, forms a strong coherent mass.

Whilst therefore the structure and the „superficial” properties of the coagulum are of little or no importance in relation to the properties after vulcanisation, they deserve attention from the standpoint of working the raw rubber and so on, as mentioned above. Methods of expressing these properties adequately in figures have however not yet been sufficiently developed, so that it is not yet possible to accurately investigate the influence of different methods of preparation in this respect, and the ultimate significance of such differences for the manufacturing processes.

In addition to the attention paid now-a-days to the vulcanising properties of the rubber, a larger interest in the structural and colloidal properties of the unchanged raw product would not be out of place.

On tests on raw rubber and the influence of some factors on the results see Chapter XX.

§ 106. Physical changes in the coagulum.

Contraction.

The coagulum, after it is formed, continues to harden; it contracts, and gradually presses out the serum. This hardening is greatest shortly after coagulation; in diluted latex the coagulum contracts more than in undiluted. In sheet-preparation, the slab in 15 % latex will begin to loose itself from the walls of the pan some hours after it is formed, whilst a slab from undiluted latex continues to fill the whole volume of the latex from which it is formed. However, a slab from dilute latex does not contract to the volume of the original, undiluted latex; when taken from the liquid, it holds more water and serum and is weaker than slab from undiluted latex.

The contraction goes on slowly under all circumstances; if one keeps coagulum for a week exposed to the air, or even under water, it becomes steadily harder and contracts more and more. Such old coagulum is often difficult to crepe. It has lost its suppleness and is torn by the mills into small pieces, which only gradually become plastic again and form a coherent crepe. The tensile strength after vulcanisation is not changed by this hardening of the coagulum, but the other properties may be greatly altered by ripening (formation of accelerators, see § 108).

Pressing and kneading.

The contraction of the coagulum, just discussed, goes on too slowly to be of any help in practice; the coagulum has to be worked mechanically to remove the larger part of the serum. When the coagulum is rolled into crepe or sheet, it undergoes a rather extensive treatment. When slabrubber is prepared, the coagulum is passed only once or twice through a widely opened mill, to press the bulk of the serum out, which else would cause a disagreeable amount of dripping and leaking.

The special features of crepeing and sheeting will be treated in Chapters IX and X. We will here discuss only some general points regarding the removal of enclosed serum by mechanical means.

The fresh coagulum contains $\frac{2}{3}$ of its weight, and even more, of serum, which continues to drip and leak out; when the water-content of the coagulum is reduced by milling to some 25 %, no further separation of liquid takes place, but the water gradually evaporates.

Whilst the fresh coagulum easily yields large amounts of the enclosed serum with the use of a small handroll or on being pressed with the hand, it is a rather curious point to note that steady pressure over a large surface does not easily drive the serum out. When a piece of fresh coagulum is put under a heavy press, there is not the regular flow of serum from it that one would expect; some serum may come out (dependent upon the way of pressing), but much less than on simple hand kneading, or on pressing

with a bottle or a rolling pin. The coagulum, under continued pressure in a heavy press, tears, eventually with small local explosions from the outer parts or from lumps that have found a way out, if the pressing takes place in some form of mould.

On closer study it will be seen that pressing the coagulum between the fingers, or between the rolls of an ordinary handmill, also does not cause the serum to come out; on the contrary, the pressed part often appears to get drier on the surface, the layer of moisture being sucked in. It is only when the pressure is released, when the coagulum contracts to return to its original form, that a large amount of serum oozes out. When a piece of coagulum is pressed between finger and thumb, the pressed part is dry; when it is released, the serum comes out first in numerous separate drops, which soon grow and form one layer of serum. In ordinary practice this is seldom noted, as the coagulum is lavishly washed during milling with a stream of water; but when sheeting on dry rolls, or even in the ordinary sheeting process, one may note that the large flow of serum does not take place during rolling, but in the first few minutes after the sheets are taken from the rolls.

In the same way, when fresh coagulum is merely stretched, the serum on its surface is sucked in and the surface becomes dry; releasing it causes the formation of drops, and soon a whole layer of serum has come out. When a fresh slab is bent, the outer surface also gets dry, whilst serum exudes from the inner parts. When the slab is bent the other way, the pressed-out serum is absorbed again, and the surface which was formerly the outer and is now compressed, exudes serum.

Thus it is explained that the coagulum does not yield the serum on even pressure, which is accompanied by a stretching; but on contracting after pressure, or on other compressions of the same nature, the serum comes out easily. Kneading or mangling — consisting in alternately pressing and releasing the coagulum — is a much easier and simpler way of getting the serum out than constant pressing. The pressing can be so arranged, for instance between pieces of cloth, that on expanding the coagulum

assumes not a shoving but a rolling movement, by which serum is then pressed out; but milling with a small handroll is, of course, much simpler.

On similar phenomena in freshly rolled sheets of Manihot-rubber see A. ZIMMERMANN, *Der Pflanze* 8 (1912), 389.

When the coagulum has lost the greater part of the enclosed serum, so that no oozing or dripping takes place, but only evaporation, pressure also will not serve to remove the rest of the serum. We made experiments with rather heavy pressures (up to 1000 Kg. per cm^2) and with coagulum containing some 3 — 10 % of moisture, and of different hardness, one or two days, or several weeks old, but found that the moisture could not be pressed out. The most probable explanation is, that coagulum with less than some 15 or 20 % of moisture shows no decrease in volume on losing this moisture; but direct proof of this explanation is still lacking.

It may be stated that even a large pressure, exercised either on dry rubber or on wet coagulum, does not effect a change in the tensile strength or rate of cure of the rubber.

See Bull. Ceyl. 27 (1916), 5, and Bull. Imp. Inst. 14 (1916), 503.

Drying under tension.

Originating probably in the conception (almost certainly false, by the way, see § 189), that Brazilian rubber owes its superior qualities to the pressure exercised on the inner parts of the ball by the outer layers, and to the tension to which these outer layers are therefore exposed, the supposition was made that exercising a certain tension on the sheets during drying — either by rolling them up under tension, or by keeping them stretched by means of a frame or weight, — would give a rubber of superior strength. As was to be expected after what was said above, the tensile strength after vulcanisation was found to be completely unaltered by such procedures.

See Bull. Ceyl. No. 27 (1916), 3, and Bull. Imp. Inst. 14 (1916), 542; 16 (1918), 427.

Slowly and rapidly drying rubber.

When wet coagulum is kept, interesting changes take place which affect the way in which it absorbs and retains moisture, and therefore its rate of drying. The fresher the coagulum, the quicker (given a certain thickness and moisture-content) it dries in the air. Keeping the coagulum overnight before rolling, either in the serum or in water, causes the rubber to air-dry somewhat more slowly; keeping the coagulum for several days, so that maturation sets in, gives a slow drying rubber. When certain parts of a sheet, for instance near the edges or the corners, are somewhat thicker, they remain wet for a longer time because of this thickness; and the wet inner part then develops the properties which we here designate as slow drying. It may take weeks to get perfectly dry and transparent, and in practice such parts are often simply cut off.

This slow drying has been ascribed by many authors to the formation of an impervious outer layer of rubber. Slow evaporation through the outer layer certainly may play a role, and the quick drying of fresh coagulum may be largely due to its porosity, or better its loose jelly-like colloidal structure, as is evident from the fact that heavily pressed coagulum dries very slowly.

These factors however are certainly not the only causes of slow drying of old or matured coagulum. When the wet layer is exposed to the air by cutting away the dry layers, or even when the wet part is cut into small pieces, and the evaporating surface is thus increased, the rate of drying is still found to be much slower than that of fresh coagulum. Not only the unchanged slabs, or the partly dried edges of sheet dry slowly, but also the crepe that is formed from them after remilling. From this it is clear that the water-retaining capacity of the coagulum changes on ageing — a phenomenon well known in other gels (studied, for instance, for silica-gels by VAN BEMMELEN).

That other factors — such as coagulation with alcohol, or the action of sulfurous acid — may also cause the coagulum or

the milled rubber to dry more slowly, was shown in § 99, 89 and 52. It may be remarked that, for instance, soaking in alkali or dilute formalin gives an increase in rate of drying, whilst soaking in water or dilute solutions of several salts or acids prolongs the drying. The mechanism of these changes is as yet unexplained.

B. J. EATON (*Agric. Bull. F. M. S.* 4 (1915), 30 and 162; *Bull. F. M. S.* No 27 (1918), 307) found that soaking in alkali accelerates the rate of drying of the rubber, and also greatly accelerates its rate of cure, but warned against the use of this method in practice, as alkali-soaked rubber is liable to get tacky and deteriorate rapidly.

CL. BEADLE and H. P. STEVENS (*VIII Int. Congr.* 9, 23; also *Z. Koll.* 13 (1913), 210) mention that rubber obtained by centrifuging the clots, which form when latex is preserved for a long time with formalin, dries very slowly. They ascribe this to the firm union of the globules, so that the enclosed moisture can escape only by passage through the rubber. However, since the clotted formalined latex was evidently kept for a long period, the time-factor already discussed (ageing) may also have played a role in this case. ' It is interesting to note that, as we found, freshly milled ordinary crepe or sheet, when soaked for some time in dilute formalin, dries quickly; a similar effect is obtained by soaking in 10% acetic acid, in 5% alum, or in alcohol. Soaking in 1% acetic acid, in 5% sodium sulphite or bisulphite, or in 1% chinisol all prolong the time of drying, whilst keeping under water for one day retards the drying markedly, and soaking for 3 or 7 days in water gives a sheet which is very slow-drying.

§ 107. Chemical changes in the coagulum.

Various chemical changes take place in the coagulum, the most important of which we shall discuss here.

The violet colouration of the coagulum by oxydation on the surface which is in contact with the air was discussed in § 12, and its prevention by anti-oxydants in § 47. It may be remarked here that this oxydation takes place in an acid medium, and that a certain degree of acidity (relatively small) and a certain concentration of the latex greatly accelerate the violet colouration. The addition

of large amounts of acid greatly delays this change or may even prevent it entirely (see § 51 and 83). In dilute latex this colouration becomes visible only much later than in concentrated latex.

See G.S. WHITBY (VIII Int. Congr. 25, 611; also I.R.J. 45 (1913), 945; also Z. Koll. 12 (1913), 155), who further stated that the discolouration was greatly intensified by adding 10 gms of calcium chloride per liter of 12 % latex (ibid. page 609).

No influence of these violet coloured substances (which by weight only constitute a very small quantity) on the inner qualities of the rubber has yet been found (see § 12).

A second change, which takes place in the air, is the formation of a yellow slimy layer, which has already been mentioned in § 94—96. This is caused by the action of aerobic bacteria (i. e. bacteria which need air for their growth) and is formed especially when coagulation is slow, for instance with small amounts of acid; though it may also develop on rapidly formed coagulum if this is kept for some time.

G. VERNET (Bull. Mars. 1 (1919), 118) observed a large bacillus of a fair degree of mobility, mostly joined in series of 2 to 4, in this slimy layer.

This yellow slimy surface-layer, when scraped from the coagulum, consists to a large extent of rubber, which has separated into floccules. If one collects this product, it can be milled into a very dark-coloured crepe, which shows inferior qualities, namely, a low tensile strength and a rather large slope, while the time of cure is noticeably (for example $\frac{1}{3}$) larger, and the viscosity practically the same as in ordinary crepe.

G. VERNET (Bull. Mars. 1 (1919), 118) found no rubber in the yellow surface-cream, when it was carefully removed. He obtained the reaction of tryptophane and, after acidifying, showed the presence of a peroxydase by guaiac and hydrogen peroxyde, which reaction did not take place after boiling.

When coagulum with such a yellow surface-layer is creped, this layer is easily washed off and removed, but some

flocks may stick to the rubber, and a crepe with dark (violet) streaks may result. These stripes are therefore due to an inferior product; but commonly this forms so small a part of the total weight, that in testing such streaky crepe no deterioration is noticeable.

See O. DE VRIES, Arch. 2 (1918), 227 and 239, who found that the addition of the slimy substance from one half of a piece of coagulum to the other half left the properties of the latter practically unchanged.

The coagulum absorbs a considerable amount of oxygen from the air, even without superficial violet-colouration occurring.

When keeping fresh coagulum in air under a glass bell, we found an absorption of gas to take place till all the oxygen had disappeared. The absorbed oxygen formed $\frac{1}{4}$ % in weight of the dry rubber; under other circumstances perhaps more of it may be taken up.

In addition to the above named changes, for which the presence of air is necessary, anaerobic processes may also take place in the coagulum. These may continue undisturbed when one keeps the coagulum under water or under serum, so that it is shut off from the air. Various processes go on at the same time, of which sometimes one, sometimes another predominates, according to circumstances.

When pieces of coagulum are kept under water or under the serum, a development of gas-bubbles soon sets in, which continues for several days. At first only about half of the gas formed is carbon dioxide, the rest consists of an inflammable gas (methane or hydrogen) and some of an incombustible one, probably nitrogen. On the following days the inflammable gas is formed in a lesser degree or not at all, and the content of carbon dioxide increases, which may then constitute 95 % and more of the gases developed. In ten days a piece of coagulum, kept in the serum, developed carbon dioxide to an extent of more than 1 % of the weight of dry rubber.

Besides these gases, the presence of small quantities of hydrogen sulphide can be easily proved, and traces of other evil smelling gases are also noticeable.

On the presence of carbon dioxide and hydrogen sulphide see also G. S. WHITBY, VIII Int. Congr. 25, 602, also I. R. J. 45 (1913), 942 and Z. Koll. 12 (1913), 150.

The formation of hydrogen sulphide from the proteins begins when the coagulum is some days old; other decomposition products (amino-acids or amines) are also formed. These nitrogen-compounds are of special importance, because amongst them are strong accelerators of vulcanisation. The result of these anaerobic changes is therefore an acceleration of vulcanisation, coupled with an increased viscosity of the rubber. The longer the time between coagulation and milling, other conditions being equal, the more rapidly the rubber vulcanises. Rubber milled on the day following coagulation vulcanises more quickly than rubber milled on the day it is coagulated, say, some hours after coagulation. This difference in time of cure amounts to 5—10 minutes. That these factors may be a source of variability in rate of cure will be shown in Chapters IX and X.

There are, however, factors which can strongly retard these changes. The effect of soaking in water will be treated in § 136 and 139, the inhibiting effect of disinfectants, such as formalin and bisulphite, has already been discussed in § 43 and 48. All these processes will be treated further in the next paragraph.

In addition to the formation of protein decomposition products, other processes go on in the coagulum of which little is known.

We have spoken above of the absorption of oxygen and the development of carbon dioxide. In practice these still little known changes make themselves felt in the fact that the non-rubber substances (and consequently the rubber) are less hygroscopic when the coagulum is kept 24 hours after coagulation, than when it is milled shortly after coagulation. This is evident from the lower moisture-content of the rubber (in crepe, for instance, 0.60 % compared with 0.70 %), and also in the fact that rubber milled 24 hours after coagulation shows a smaller weight than when milled shortly after coagulation. In crepe this difference in weight amounts to about $\frac{1}{2}$ % and in sheet it may amount to 1 % (see § 128 and 150).

§ 108. Maturation of the coagulum.

Usually the coagulum is milled before the above mentioned changes have proceeded very far, although the differences are great enough to decrease the uniformity in rate of cure to a considerable extent, when the time between coagulation and milling and other factors in preparation are not kept constant (see § 117 and 135).

If one keeps the coagulum longer, whether accidentally, when by some cause (breakage in the factory etc.) one gets behind with milling, or intentionally, in order to produce a rapidly vulcanising rubber, then these changes go further and one gets matured coagulum. The most important change is a large increase in the rate of cure, which may become two or more times as great. At the same time the viscosity increases, the tensile strength is somewhat improved, and the slope becomes less (better).

The preparation of matured rubber on a large scale will be treated in § 192. For some examples of rubber matured by accident in actual practice (breakage of machinery, theft of coagulum which had then been concealed in the wet state etc.), see O. DE VRIES, Arch. 2 (1918), 230 and 240.

The largest changes in this direction take place in coagulum that is spontaneously coagulated; of this the following figures may serve as an example.

	Tensile strength	Time of cure	Rate of cure, ratio	Slope	Viscosity
Average for ordinary crepe . . .	1.37	116	100	35.8	31
Matured after spontaneous coagulation	1.41	50	232	32.5	64

The time of cure is therefore reduced to less than $\frac{1}{2}$ of that for ordinary crepe. In some cases an even greater rate of cure was reached, and the crepe prepared from

matured coagulum vulcanised in only 40 or even 30 minutes, that is in only $\frac{1}{4}$ the time of ordinary crepe.

Tensile strength, slope and viscosity are all better for the matured rubber; maturing of the coagulum therefore changes all the above mentioned properties in a favourable direction.

For tensile strength however the increase is probably not due to any intrinsic improvement in the rubber, but solely to the shorter time the rubber is exposed to the high temperature of vulcanisation, see § 204.

Coagulum prepared with acetic acid too undergoes important changes in properties, as is shown by the following figures.

	Tensile strength	Time of cure	Rate of cure, ratio	Slope	Viscosity
Normal crepe. . .	1.37	116	100	35.8	31
Crepe from coagulum ripened after acetic acid coagulation . . .	1.41	75	155	33	53

It will be seen that the changes in time of cure and viscosity are somewhat less, because the acetic acid has acted to some extent as a disinfectant and retarded the maturation caused by micro-organisms.

For details of the figures given above, obtained according to our method of testing, see O. DE VRIES, Arch. 2 (1918), 213 and 235.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F.M.S. No. 27 (1918), 388) give the following average figures:

	Breaking load	Optimum time of cure	Rate of cure, ratio
Slab	1.51	1 $\frac{1}{4}$ hours	260
Smoked sheet .	1.46	2 $\frac{3}{4}$ "	118
Thin pale crepe.	1.30	3 $\frac{1}{4}$ "	100

that is, slab vulcanises in only $\frac{2}{5}$ the time of average plantation-rubber. About the figures for tensile strength see however § 204 and 224.

Excess of acetic acid was found by these authors to decrease the rate of cure after maturation; 1.7 times the minimum amount of acid decreased the rate of cure by 10%, five times the minimum by 26%.

H. P. STEVENS (Bull. R.G.A. 1 (1919), No. 1, page 41) found the following figures for rate of cure (expressed as percentage of the average for crepe or sheet) for matured rubber, when coagulated with increasing amounts of acetic acid:

1 part of acid in 1200 parts of latex:	171%
4 parts " " " " " " "	129 "
8 " " " " " " "	112 "
16 " " " " " " "	88 "

The effect of acid, working here to retard or inhibit maturation, is clearly seen.

The same author (Bull. R.G.A. 1 (1919), No. 2, page 42) found the difference between matured rubber, coagulated spontaneously, and that coagulated with a small amount of acetic acid to be negligible, the acetic acid coagulum curing sometimes faster than the spontaneously coagulated,—in contradiction to our results, where spontaneous coagulation always gave a quicker curing matured rubber. The conditions governing maturation, and the processes which compose it, will have to be studied in greater detail, to determine which are the factors (degree of infection?, temperature?) responsible for such differences in results.

Whilst the properties after vulcanisation show such marked changes, the composition of the rubber may also be expected to be changed by the decomposition of serum-substances; but data are still scarce. The nitrogen-content may diminish markedly (to $\frac{2}{3}$ or less), but the figures on the ash- and resin-content are contradictory.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 97) found the nitrogen-content in matured slab diminished to 0.30 or even 0.21 %, as compared with 0.45 % in ordinary smoked sheet or crepe; in the interior of the slab as little as 0.10 % nitrogen was found.

H. P. STEVENS (J. S. Ch. I. 36 (1917), 366) found the nitrogen-content in crepe or unsmoked sheet 0.46 %, against 0.38 % in unrolled slab, and 0.30 % in creped matured slab.

It is however worthy of remark that both EATON c.s. (Bull. F. M. S. No. 27 (1918), 97) and STEVENS (l.c.) found the

nitrogen-content in smoked slab exactly the same as in smoked sheet and smoked ordinary crepe, though the rate of cure had increased very much, so that the loss in nitrogen seems not to be indissolubly connected with the decomposition which causes an increase in rate of cure. It should, however, be taken into account that the surface-layers of the slab contain a much larger proportion of nitrogen than the interior (0.6 against 0.3, or 0.3 against 0.1 %).

In the samples prepared by L.E. CAMPBELL (Bull. Ceyl. 35 (1917), 13 and Bull. Imp. Inst. 16 (1918), 435) the matured rubber (after washing and drying) showed 0.15 to 0.47 % (that is $\frac{1}{14}$ to $\frac{1}{5}$) less „protein” than the controls; the percentage of resin was from $\frac{1}{2}$ to $1\frac{1}{2}$ % higher. The differences in ash-content were not marked. The matured rubbers, on washing and crepeing, showed a loss in protein of up to 0.3 %, as compared with less than 0.1 % when washing ordinary rubber, and 0.6 %, when washing rubber obtained by evaporating latex to dryness.

On the contrary, in some samples of crepe from matured slab we found the ash-content higher, the acetone-extract lower than in the control (Arch. 2 (1918), 230 and 239). What differences in method of preparation are the cause of these divergencies, is as yet unexplained.

An analysis of creosoted matured rubber is given by J. C. WILLIS and M. K. BAMBER (Circ. R. B. G. 4 (1907), 3; also Trop. Life 3 (1907), 57), who found the ash-content much lower, and the proteins much higher than in average Ceylon biscuit.

The decomposition of serum-substances makes itself felt in the weight of the rubber obtained after maturing, which is considerably less than in ordinary preparation.

In a number of small-scale experiments we found the crepe from matured coagulum to weigh 2 to $2\frac{1}{2}$ % less than ordinary crepe from 15 % latex, rolled the day after coagulation (see O. DE VRIES, Arch. 2 (1918), 213 and 235). The difference in weight in preparing matured rubber on a large scale was found to be $1\frac{1}{4}$ % in one series. Besides the loss caused by decomposition of serum-substances during maturation, an additional loss by incomplete coagulation, milky serum etc. may occur in practice.

That the physical conditions of the coagulum also change during maturation, makes itself evident by the fact that matured slab, or the crepe prepared from it, dries slowly. Coagulum that is only slightly rolled to a slab of 1 or $\frac{1}{2}$ inch thickness retains some 10 % of moisture

indefinitely, without becoming dry in the interior, when kept in the air; crepe prepared from such coagulum is also slow-drying (compare § 106) and takes several weeks to air-dry.

The preparation of matured rubber on a large scale in estate-practice will be treated in § 192; the nature of these changes will be discussed here.

The investigations on this point are principally due to B. J. EATON and his co-workers, who worked out and proved the theory that the increase in rate of cure is due to a decomposition of the nitrogen-compounds (proteins) in latex by micro-organisms, the decomposition-products being accelerators of vulcanisation.

This theory was first advanced by B. J. EATON in 1915 (Agric. Bull. F.M.S. 3 (1915), 202), and further proved in subsequent papers (Agric. Bull. F.M.S. 4 (1915), 1 and 58; *ibid* 6 (1917), 148 and 315; J.S.Ch.I. 34 (1915), 989; *ibid* 35 (1916), 715 and 36 (1917), 1217. We will not treat this subject *ad fundum*, nor quote the work of EATON *c.s.* in every instance, as the reader finds a complete review of their investigations in „Preparation and Vulcanisation of Plantation Para Rubber” by B. J. EATON, J. GRANTHAM and F. W. F. DAY, Bull. F.M.S. No. 27 (1918).

That the maturation-processes are caused by micro-organisms, is apparent from the following facts:

1) Disinfectants, when added to the latex, retard or wholly inhibit these changes; when acting on coagulum immersed in them, they retard maturation, and when the coagulum is removed from the disinfectants, a maturation may set in.

Under this head may be brought:

acetic acid, the effect of which was already treated above; bisulphite, which retards the beginning of maturation in coagulum rolled the day after coagulation (see § 48), retards spontaneous coagulation by bacterial action, and also retards the maturing processes;

formalin, which retards maturation either when added to the latex prior to coagulation; or when used in soaking the coagulum. Once, however, the accelerator has been formed, soaking in formalin only slightly retards the

cure, due to the action of formalin itself as a negative catalyst (see § 43).

smoke, which may retard maturation, but does not do so in all cases. In smoked slab (and in smoked balls, see below and Chapter XIV), maturation goes on. Smoking the already matured rubber greatly decreases the rate of cure, either because the smoke-constituents act as retarding agents, or because they destroy or alter the accelerators already formed.

alcohol, which also acts in this way; after coagulation with alcohol (see § 99) the clot shows no increase or only a small one in rate of cure on keeping.

many other chemicals (coagulants such as sulphuric acid, alum, tannic acid; all anti-coagulants and disinfectants, and so on), which have a smaller or larger disinfecting action and may partly or wholly inhibit maturation.

It is however, interesting to remark that not all disinfectants inhibit maturation. So, for instance, when creosote is added to the latex, maturation may proceed; phenol or cresol, added to the latex, do not change the rate of cure of the matured rubber, and the use of β -naphtol, which inhibits the putrefactive changes that cause the bad smell, but which allows the formation of accelerators to go on, has even been patented as a special method of preparing matured rubber.

Under the same head may probably be brought the action of smoke in the preparation of Brazilian balls (see § 190), which retards but does not inhibit maturation.

On the use of creosote to inhibit putrefaction or mouldiness see § 46. Creosoted coagulum was found to show a considerable increase in rate of cure on keeping in the wet state in the experiments of L. E. CAMPBELL (Bull. Ceyl. 35 (1917); Bull. Imp. Inst. 14 (1916), 547 and 16 (1918), 426). For the action of phenols, see EATON c. s. Bull. F. M. S. 27, page 25 and 295; for patents on the use of β -naphtol see I. R. J. 56 (1918), 122; J. S. Ch. I. 37 (1918), 313 A.

2) Heat favours maturation up to a certain degree; the most favourable temperature seems to be 50° C, whilst higher

temperatures retard or wholly inhibit maturation by killing the micro-organisms.

3) Cold may inhibit maturation wholly; when the coagulum, after being kept for some time in the cold (some 5° C), is again brought to the ordinary temperature, the maturing processes start again and may lead to a rubber which cures as rapidly as when matured directly after coagulation.

4) The moisture-content of the coagulum is a *conditio sine qua non*, and determines how long maturation can proceed. In so far as it affects the moisture-content, the thickness to which a piece of coagulum is rolled out affects maturation also, and the rate of drying, more precisely the period during which the rubber contains enough moisture to mature, is a further point of importance.

The lowest moisture-content, at which maturation is possible, has not yet been determined; it will probably be found to lie in the neighbourhood of 10 %.

That it is the non-rubber constituents that are attacked in the first place by the micro-organisms, is evident; this is corroborated, for instance, by the fact that dilution of latex does retard the rate of cure of matured slab prepared from it. Matured rubber from 15 % latex may, for instance, cure 70 % more slowly than that from 30 % latex.

Whilst keeping the coagulum in the serum for several days gives nearly the same maturation as keeping in the air, keeping the coagulum in water, by which a large amount of serum-substances may be extracted, gives at first a marked decrease in rate of cure (see § 136), but does not prevent maturation, which sets in after some time. The high rates of cure of fully matured rubber are however by no means reached, not even when the coagulum is kept for a long time in water. When the coagulum, after having been soaked in water for some time, is kept in a moist state in the air, maturation may set in to some extent, but often does not proceed fully, as in the case of inhibition by cold (see above), so that the extraction of soluble serum-substances makes itself felt.

Soaking matured rubber (either the slab, or the crepe formed from it) in water, does not decrease the rate of cure, so that the accelerator, once formed, is not extracted from the rubber by simply keeping it in water, as little as it is extracted by washing and crepeing the matured slab.

Keeping freshly rolled crepes in water, however, also gives an increase in rate of cure. The effect of extraction with water will have to be studied further, qualitatively and quantitatively, to explain these phenomena fully.

See O. DE VRIES, Arch. 2 (1918), 220 and 238; *ibid* 3 (1919), 359 and 373.

It may be regarded as proved that maturation is caused by the action of anaerobic micro-organisms; these organisms have however not yet been isolated and determined.

H. P. STEVENS, in samples prepared by S. MORGAN (Bull. R. G. A. 1 (1919) No. 2, page 42) found the rate of cure to be only slightly influenced by effecting the coagulation and maturation in the air, or in the absence of air. It may perhaps be assumed that the air does not penetrate deeper than the surface-layer, where putrefactive organisms form the slimy layer treated in § 107, which is removed when taking the coagulum out of the vessels.

It was stated above that keeping the coagulum in the air (for instance on a board) gives rubber of the same properties as maturing it immersed in the serum.

G. VERNET (Bull. Mars. 1 (1919), 121) discussed the desirability of effecting maturation by specially cultivated micro-organisms, and — if Brazilian rubber is in this respect superior — by strains of the best maturing micro-organisms from Brazil. No facts are, however, as yet available to lend support to this proposition.

That it is chiefly the proteins that play a role in these processes, and that such protein-decomposition products as amines or amino-acids are the accelerators formed, is very probable from the well-known properties of these substances as accelerators. Ordinary proteins such as casein, peptone, or protein from serum (see § 112), when added to the rubber, are not accelerators; but when they have been decomposed first, they accelerate the rate of cure markedly (see also § 112 and 246).

The decomposition-products that are formed during these

processes have, however, not yet been identified, and little is known as to the quantity in which they are present in rubber matured to different stages, or as to the amounts that produce a certain increase in rate of cure.

H. P. STEVENS (J. S. Ch. I. 36 (1917), 368) isolated basic amines by extracting ordinary crepe and crepe obtained from matured slab with water or dilute sulphuric acid; he found the extractable quantities to be very small (much less than 0.1 % of the rubber), though considerably larger in the crepe from matured rubber.

The opinion has been expressed that complete maturation leads to a rubber very uniform in rate of cure. In general it may be expected that a biological process, such as maturation, will be influenced by many external circumstances; and the probability is great that it will lead to a variable rather than to a uniform product. However, circumstances on estates may in most cases be such that maturation, when sufficiently prolonged so that it is complete, leads to a sufficiently uniform product.

See B. J. EATON, Agric. Bull. F. M. S. 5 (1917), 183.

In how far this is the case, can only be determined by a large number of experiments with latex from different sources, and under different circumstances. In judging the results it should not be forgotten that the differences in time of cure would have to be expressed on a percentage-basis; 5 minutes difference on a time of cure of 50 minutes means 10 % variation, but in ordinary sheet or crepe, curing in 100 minutes, it is only 5 %.

Several conditions, which it would not be possible to avoid when preparing matured rubber on estates, cause differences in its rate of cure. For instance, dilution of the latex may change the time of cure from 50 to 80 minutes; diluted latex from a rainy day gave us matured slab with a time of cure of even 120 minutes.

See O. DE VRIES, Arch. 2 (1918), 218 and 237.

Further the temperature may be expected to have an influence, so that on low lying estates the maturation process will be probably easier than on high estates.

We found that the abnormal latex, obtained when opening a tapping cut (see § 29), which gives a slow-curing rubber, also gives on maturation a much slower rate of cure than ordinary (f. i. 100 minutes instead of 50).

See O. DE VRIES, Arch. 2 (1918), 217 and 237.

In samples of matured rubber prepared on different estates the rate of cure may vary over a large range, say from 40 to 100 minutes, and is far from uniform; so that estate conditions, often difficult to standardise, may have a large influence on maturation, as was to be expected for a biological process.

EATON c.s. (Bull. F. M. S. No. 27., page 345) found the rate of cure for slabs from different estates to vary from $\frac{1}{2}$ to 2 hours.

O. DE VRIES (Arch. 2 (1918), 235) in a series of 9 samples prepared in the laboratory found the time of cure to vary only from 80 to 95 minutes, not much more than in the controls (130 to 145); in another experiment the matured rubber varied from 50 to 60 minutes and was therefore also fairly uniform. Samples from different estates (*ibid.* 229 and 239), however, showed times of cure from 50 to 100 minutes.

H. P. STEVENS and S. MORGAN (Bull. R. G. A. 2 (1920), 68) found the rate of cure of seven samples of matured rubber, prepared on different days either from undiluted latex or from latex diluted to standard rubber-content, to show four times the variation of ordinary crepe prepared by acetic acid. Calculating the average deviation as percentage of rate of cure, the matured rubber showed a variation 2 to 3 times as large as that of the control.

CHAPTER VIII.

THE SERUM.

§ 109. Practical importance of serum.

In actual estate-practice the serum has the character of a waste-product. The serum in the coagulating tanks or pans is thrown away when the coagulum has been taken from it, and the serum which is contained in the wet coagulum disappears with the wash-water in milling. It is only in judging whether coagulation was complete, that the serum has for a moment the attention of the planter: milky serum meaning a loss in rubber.

The serum may have some practical importance for saving acetic acid, for keeping the lower grades in, and for diluting the latex. We treat this in § 85 and 185, 70 and 114.

From the standpoint of research it has received a great deal of attention, as it is easier to analyse than the latex, in which the bulk of rubber hinders all operations, and which, as an unstable liquid, is more difficult to handle. The serum therefore is often used to get a preliminary insight into the changes in composition of the latex, and perhaps more is known of it than of the latex itself. There is often even some confusion in present literature, as data obtained by investigating the serum are quoted as representing the composition of latex, which, of course, is unallowable as long as the amount of non-rubber constituents, that were carried along with the rubber in coagulation, is not determined.

§ 110. Preparation of serum.

The great difficulty in investigating Hevea-latex and serum is, that the rubber and serum cannot be separated in their original state, for instance, by physical means as centri-

ugation. Coagulation by means of chemicals, heat or other means is necessary; but this may alter the composition of rubber and serum. „Natural” or spontaneous coagulation would give still larger deviations, because of the decomposition of serum-substances that accompanies it.

The serum obtained after coagulation with acetic acid may, apart from the presence of acetic acid, have a composition other than the original serum, some constituents perhaps having been rendered insoluble and coagulated with the rubber, others having perhaps been decomposed by the acid or dissolved from the rubber and carried into the serum. Coagulation with alcohol may give serum of another composition, and so on.

Though this point should never be lost sight of in researches on the composition of latex and serum, the differences, at least in certain respects, are not so large as to be of importance in estate-practice. For instance, the specific gravity of serum, after coagulation with increasing amounts of acetic acid, is found to be practically the same (when recalculating on acid-free serum); but the total solids in the serum and the ash seem to increase somewhat with increasing amounts of acid.

O. DE VRIES, Arch. 3 (1919), 189 and 204.

In so far as, in the following, figures are given for the composition of serum without further details, they relate to serum obtained by coagulating the latex per 100 cc. with 20 cc. 2½ % acetic acid, and recalculating on original serum or latex. For details see O. DE VRIES, Arch. 3 (1919), 189, 204 and 418.

E. FICKENDEY (Z. Koll. 8 (1911), 45), for *Funtumia* latex, recommends freezing the latex for the preparation of pure serum.

§ 111. Composition of serum.

The serum is a clear slightly yellowish liquid with a distinct acid reaction, caused as well by the acid used for coagulation as by the acids formed spontaneously in the latex, the amount of the latter often surpassing that of the acid added.

The chief constituents of the serum are mineral substances, proteins, quebrachite and sugars, to which several other constituents of unknown composition must be added.

The rough distribution of the non-rubber substances in

coagulum and serum from normal latex is given on page 14. The composition of original serum may be taken to vary between the following limits.

	Normal	Variation
Total solids	5	4 — 5.5
Ash	0.8	0.5 — 0.9
Nitrogen	0.1	0.05 — 0.15
Quebrachite	2.25	1.5 — 2.5
Reducing sugars	0.35	0.25 — 0.5

The specific gravity varies between 1.016 and 1.025, and for ordinary latex lies in the neighbourhood of 1.023 (see § 15).

In an analysis of latex from a 32 year old tree at Singapore (Agric. Bull. Str. F. M. S. 9 (1910), 51), which on coagulation with acetic acid gave 36.29% rubber, the serum contained 4.13% total solids, of which 3.61% organic matter and 0.52% ash.

K. GORTER (Arch. 1 (1917), 376) from a latex containing 37.0% of rubber and coagulated per liter with 600 cc. water in which 2½ cc. acetic acid was added, collected the clear serum and found:

	Calc. on 100 cc. latex	Calc. on 100 cc. orig. serum
Total solids	2.91	4.62
Ash	0.53	0.84
Protein ($N \times 6.25$)	0.34	0.54
Quebrachite.	1.45	2.30
Sugars	0.25	0.40

The sugars were determined by Fehling's solution after inversion, the quebrachite was calculated assuming that the total rotation of the serum might be ascribed to the quebrachite. Assuming the reducing sugars to have been present in the form of saccharose, and correcting the total rotation for that effect, the figures for quebrachite would change to 1.66 and 2.54%, but then the laevo-rotatory power of the proteins in serum is not taken into account, so that 1.5 and 2.4% will be approximately the right figures.

The mineral constituents of the ash are the same as those of latex (see § 4); about the amount in which the different constituents are present, and about the changes in composition of the ash under different circumstances, nothing is as yet definitely known.

The serum contains a certain proportion of nitrogenous matter, which may be put at $\frac{1}{3}$ of the total present in the latex, as the table on page 14 indicates. Part of it is present as a soluble protein, which separates in white flocks on moderately heating the serum. This precipitate forms $\frac{1}{6}\%$ of the original serum after coagulation with acetic acid, and $\frac{1}{4}\%$ when the rubber is coagulated with alcohol. The greater part of the nitrogen components therefore remains dissolved in the serum even after heating it and, unless decomposed or evaporated, must be found in the brown, sticky residue after evaporation.

G. A. VERNET (Ann. Mars. 27 (1919), 1) mentions that the proteins in latex have laevo-rotatory power, which has to be taken into account when determining quebrachite or sugars by the rotation of light, for instance, by first precipitating the proteins by alcohol.

The presence of quebrachite and reducing sugars in the serum is also indicated by the table on page 14. In ordinary crepe or sheet very little of them seems to remain in the rubber, and the bulk is found in the serum, to which it gives a laevo-rotation, which increases after inversion of the sugars (for instance, by heating the acid serum).

The composition of serum is influenced by many factors. The specific gravity and total solids decrease, and the ash increases with heavy tapping and other such factors (see § 32, page 70). Serum of latex from trees that have had a period of rest shows a high specific gravity and a high content of solids, but a low ash-content (see § 29, page 65); and so there are other factors, mentioned in Chapter II, which affect the composition of the serum. About the most important constituents, however, viz. the accelerators present in latex and serum, very little is known. As to the quantities in which they are contained in the serum, and the changes they undergo due to the

action of different factors, exact data are still absolutely lacking, so that conclusions — so necessary in order to decide on the most rational system of preparation — cannot be based on certain knowledge of that point.

§ 112. Accelerators in the serum.

That the serum contains an accelerator (or different accelerators) is apparent from — and offers an explanation of — the following facts:

1) The residue obtained by evaporating the serum to dryness accelerates vulcanisation.

B. J. EATON and J. GRANTHAM (J. S. Ch. I. 35 (1916), 725; also I. R. J. 52 (1916), 307; Bull. F. M. S. No. 27, 93) found that the dried residue from serum (from which the protein precipitated by heating had been removed) accelerates vulcanisation. Added in an amount of 1.33% to the rubber, it reduced the time of cure to 85%; an addition of 13.3% caused the time of cure to decrease to 62%. Increasing amounts of this residue had the following effect:

Amount of serum-residue added, in % of rubber	Time of cure, ratio
0	100
2.2	82
4.4	73
6.6	68
8.9	64
11.1	64

H. P. STEVENS (J. S. Ch. I. 36 (1917), 369) found an addition of 1.67% of the rubber to decrease the time of cure to appr. 80%; when added to „protein-free” rubber, the accelerating effect was, however, much greater (ibid. 367).

In complete concordance with these investigations we found the time of cure, on adding 1% of the dry-residue of serum, from which the flocky protein-precipitate had been removed, to decrease from 100 to 85 minutes, whilst tensile strength and slope remained the same.

2) Rubber prepared by evaporating the latex to dryness, so that it contains all the serum-substances, vulcanises more rapidly (see § 102):

It is interesting to note that the substance, ordinarily

remaining in the serum, which causes this greater rate of cure in dried-up latex, is not washed away by subsequent crepeing, so that, once incorporated in the rubber, it seems to have lost its easy solubility.

The bearing of this point on rubber prepared according to special methods (Brazilian method, Kerbosch process) will be treated in Chapter XIV and § 193; in such cases, besides the content of serum-substances, the coagulation by heat, the maturation, and other factors may play a role, and the special influence of the serum-substances is not so easy to determine.

When the film of latex is too thick and dries slowly, maturation sets in, and the rate of cure increases (see § 102).

3) Latex rapidly dried up to a film on a porous plate, so that part of the serum-substances are absorbed by the plate, gives a rubber that vulcanises much more slowly than one containing all serum-substances.

B. J. EATON and J. GRANTHAM, J. S. Ch. I. 36 (1917), 1224; Bull F. M. S. No. 27, 80.

4) Dilution of latex with water gives a slower-curing rubber. The rubber, from dilute serum, absorbs less of the soluble serum-constituents, with the result that the coagulum is somewhat less in weight (see § 128 and 150) and vulcanises more slowly (see § 64).

5) Diluting the latex with serum does not change the rate of cure of the rubber. For instance, when crepe from undiluted latex (33 % rubber) vulcanises in 105 minutes, dilution with serum and water gives the following times of cure:

Diluted to a rubber-content of	15 %	7½ %
Time of cure, when diluted with serum	105	110
" " " " diluted with water	120	125

On dilution with water, therefore, the ordinary retardation in cure, already treated in § 64, takes place; on dilution with serum the time of cure remains nearly constant (the small difference at the 7½ % dilution being probably due to the fact that the serum obtained after acetic acid coagu-

lation has not wholly the same composition as original serum). A further proof that it is the concentration in serum-substances of the mother liquid, from which the rubber-globules are coagulated, which determines the absorption of such substances and thereby the rate of cure of the rubber, is obtained by diluting the latex with both serum and water, so that the rubber-content of the final liquid is $7\frac{1}{2}\%$, but the composition of the diluted serum the same as in latex diluted with water to 15% . The time of cure of the crepe was found to be somewhat less than 120 minutes, the same as of crepe from latex diluted with water to 15% .

The coagulum in these experiments was rolled a few hours after coagulation, so as to prevent maturation. The serum was obtained by coagulating a large quantity of latex in the ordinary manner with acetic acid. Of course, this serum has not exactly the same composition as original serum, but is somewhat diluted with water and acid.

It is to be remarked that, when the coagulum is rolled next day, maturation begins, and is found to proceed more rapidly in latex diluted with serum than in undiluted latex, so that in such a case the rate of cure, on dilution with serum, is no longer constant.

6) In partial coagulation the first clot, which contains a large proportion of non-rubber substances, also seems to carry more accelerating serum-substances, as it vulcanises more rapidly than the rest.

See § 176 and O. DE VRIES, Arch. 1 (1917), 185.

Whether the accelerator, which is thus absorbed by the first clots that are formed, is the same as or related to the one that remains in the serum and is found in the dry residue, is not yet known.

Whilst therefore the fact that the serum contains an accelerator or accelerators may be regarded to be proved beyond doubt, the nature and composition of the accelerators is not yet completely established.

The proteins, which are precipitated from the latex on heating or on keeping, do not accelerate vulcanisation, and the accelerator is therefore not to be sought among them.

B. J. EATON and J. GRANTHAM, J. S. Ch. I. 35 (1916), 725; also I. R. J. 52 (1916), 307; Bull. F. M. S. No. 27, 90. We can confirm this observation as well for the protein-precipitate from acetic acid serum, as for that after coagulation with alcohol.

H. P. STEVENS (J. S. Ch. I. 36 (1917), 367) gave the following further details on the action of these proteins. They do not cause an acceleration in ordinary rubber, containing the usual proportion of protein; but when added to rubber which is freed from the protein by dissolving in benzene, filtering and recovering, the protein precipitate from serum accelerates the cure, or better restores the lost rate of cure.

When the protein-precipitate is kept in a moist state, so that decomposition sets in, an accelerator is formed in it (B. J. EATON and J. GRANTHAM, l. c.).

The accelerator therefore has to be looked for in the brown sticky mass, which is obtained by evaporating the serum to dryness and in which it is indeed found, as we saw under 1 above.

Amongst the serum-substances the largest in bulk, viz. quebrachite, is not an accelerator, and even somewhat retards the rate of cure of „protein-free” rubber.

H. P. STEVENS J. S. Ch. I. 36 (1917), 367.

By precipitation with phosphotungstic acid, basic amines which have a marked accelerating effect may be isolated from the serum-residue in a small quantity.

H. P. STEVENS (J. S. Ch. I. 36 (1917), 369) found that an addition of 0.16 % (calc. on the rubber) of the bases isolated from concentrated serum accelerates the cure nearly as much as 1.67 % of serum-residue; 0.66 % of base (on the rubber) caused barely the double effect.

Whether the basic accelerators present in serum are the same as, or closely related to, the protein-decomposition products formed during maturation, is not yet cleared up. It also remains to be investigated, whether the serum-residue contains other accelerators than these amines, especially whether some of the mineral components (or salts of organic acids) have an accelerating effect.

§ 113. Changes in the serum.

The serum is not a stable liquid; on the contrary all kinds of changes take place. The formation of acids in the

serum, causing the natural acidity of latex, was treated in § 13 and 94—96. Other changes belong to the maturation-phenomena taking place in wet coagulum; they have been treated in § 108, and principally consist in a decomposition of serum-substances (in the first place proteins and sugars) with development of gases (carbon dioxide, hydrogen sulphide, and so on) and accelerators. The total solids in the serum are, of course, decreased by such decomposition, and the specific gravity also.

For serum after coagulation with 10 and 5 cc. 2½% acetic acid per 100 cc. latex the following figures (calc. on original serum) were found, when investigating it 2 hours and 22 hours after coagulation:

	Specific gravity	
	after 2 hours	after 22 hours
10 cc. . . .	1.0220	1.0205
5 cc. . . .	1.0219	1.0202

From this the decrease in specific gravity (total solids), when the coagulum and serum are left for 24 hours, is apparent (O. DE VRIES, Arch. 3 (1919), 190).

B. J. EATON and F. W. F. DAY (Agric. Bull. F. M. S. 4 (1916), 351; Bull. F. M. S. No. 27, 101) found that the nitrogen-content of a dilute serum from 0.06% decreased in 10 days to 0.04, and in 60 days to 0.03%.

For keeping the serum for investigation we found an addition of formalin (f. i. 1%) the most suitable; some of the protein may separate in flocks, but specific gravity, dry substance and ash remain constant during several weeks. Chloroform is also an effective disinfectant, but as it dissolves only partly in the serum, recalculations are not so simple as in the case of formalin. When such precautions are omitted, the investigation of serum after keeping it some time may give misleading results; and figures for serum from coagulum that is rolled the day after coagulation may already differ appreciably from those of fresh serum, as we saw above.

When the serum is kept, for instance, in closed bottles, a precipitate is generally formed, consisting chiefly of proteins, which we treated in § 112.

Keeping the serum for some days gives rise to decomposition-processes by which accelerators are formed, and by soaking freshly rolled ordinary crepe in such serum its rate of cure may be accelerated.

For instance:	Standard time of cure
ordinary crepe	120
soaked in 7-day-old serum for 2½ hours	> 100
" " " 24 "	95
soaked in water for 2½ hours	120
" " " 24 "	120

In another experiment a more rapid-curing crepe (from spontaneous coagulation) was brought from 95 minutes to 75. The rapid cure of completely matured rubber is however not reached by this procedure.

When dilute serum (for instance, water in which freshly rolled sheets have been soaked) is kept in the air for some days, a jelly-like substance, floating in the liquid, may be obtained, as though some „fat” had been extracted from the rubber. This substance is formed by the action of micro-organisms.

§ 114. Use of serum.

The acid serum is sometimes used in coagulation either by itself or to dilute the acetic acid. We treated this method of saving acetic acid in § 85, where the addition of sugar to the serum (to increase its acidity) was also mentioned.

The serum may further be used to soak the lower grades and help to prevent oxydation and discolouration; some data on this procedure will be found in § 185.

Whether the use of serum of the foregoing day, instead of water, to bring the latex to standard dilution (by which procedure a higher degree of uniformity in rate of cure might perhaps be reached than with present methods, see page 255) will gain any practical importance, remains to be seen. The uniformity obtained by carefully following the present

standard-methods seems to be more than sufficient to meet the demand; and further the use of serum has some practical drawbacks. It has to be filtered carefully, or else the flocks of rubber or the precipitate of proteins formed on standing during the night may cause streaks or spots in the rubber; and the smell of serum, when a beginning of decomposition sets in, may be less agreeable and convey an idea of decay, though this, in the case of rubber, is quite wrong (compare § 196), since the protein-decomposition products are accelerators and favourable catalysts.

§ 115. Milky serum, losses of rubber.

When coagulation is properly carried out and sufficient acid is used, the coagulum leaves behind a serum which is as clear as water, though somewhat yellow in colour.

In sheet-preparation especially one often wishes to secure a clear serum within a few hours, because this gives the best guarantee of the formation of a good stiff coagulum. If, however, one wishes to save acid, then it is necessary to consider carefully how far one can go, and when a loss of rubber in the serum takes place.

Whenever there are flocks or clots in the serum, which are lost in milling, there is certainly a loss of rubber. Opaque, opalescent serum however does not always indicate a loss of rubber. When the serum is half transparent, the cloudiness is mostly caused by proteins or similar substances. If one allows such serum to stand, floccules will separate out and sink; these for the greater part are not rubber, since rubber floats in the serum. It is only when the serum takes the colour of dilute milk, that there is a real loss of rubber. Serum which is quite white, but which has no floccules floating in it, if kept, will give a sediment amounting to 1 to $1\frac{1}{2}$ gms per liter. Of this $\frac{1}{2}$ to $\frac{1}{3}$ may be protein, which also separates out from clear serum. Hence the loss of rubber may be some $\frac{1}{2}$ or $\frac{2}{3}$ gm per liter of latex, which in price is about equal to 0.3 cc. of acetic acid, so that in such cases the cost of more acid to secure the last bit of rubber from the latex just balances the gain in rubber.

In crepe-preparation especially, where it is not so important that the coagulum be smooth and well formed, one does not need to be so concerned with a slight cloudiness in the serum, if only one is certain that latex and acid have been well mixed from bottom to top and in all corners of the tank, so that all the acid added is used efficiently.

Some experts regard the occurrence of a slightly milky serum, caused occasionally by slight variations in the daily procedure, as an indication that the proportion of acid is well (economically) chosen, being just above the minimum. Strictly standardising coagulation, so that the serum always has the same appearance after the use of the same amount of acid, is, of course, a still surer method.

CHAPTER IX.

PREPARATION OF CREPE-RUBBER.

§ 116. Form and hardness of the coagulum.

As the coagulum, in the preparation of crepe, is completely torn up, the *form* of the pieces that enter the first mill is of no importance. The latex is generally coagulated in bulk, either in one large tank (often in the mixing tank) or in glazed earthenware (Shanghai) jars of 200 to 250 liters. To feed the first mill, large lumps are simply torn from the bulk of the coagulum by hand, or thick slices are cut from it by a knife. This is easy enough when the coagulum is not too hard; for instance, when milling is begun in the afternoon, a few hours after coagulation, or (when milling next morning), when the latex had been diluted to, say, 15 % rubber-content. The coagulum from undiluted, or even 25 % latex, when kept overnight in the serum, is rather hard, and in such a case the use of wooden partitions in the coagulating tank is to be recommended, so as to obtain slices of a suitable thickness (f.i. two inches). Some estates, not in the possession of a strong enough macerator, even prefer to coagulate in enamelled or wooden pans, just as in sheet-preparation, so as to get flat slabs of coagulum that are easily workable in their mills.

The *hardness* of the coagulum is of little importance, when the first machine is strong enough; with small machines, or a shortage in engine-power, a weak coagulum is preferred, which may be obtained by the methods indicated above. Even with strong mills one can save much time and energy by so proportioning latex, acid, and water, that the resulting coagulum is neither too hard nor too soft, so that the tearing by hand or knife proceeds easily and quickly. The fact that this hardness or weakness is of no importance for the

strength of the resulting rubber, was dealt with in § 106. When a weak coagulum is obtained by dilution of the latex, the content of serum-substances changes, and the rate of cure and viscosity may diminish by this secondary reaction, as treated in § 64. Keeping the coagulum after coagulation, by which it becomes harder, also gives a small increase in rate of cure in a secondary way (by beginning maturation), which will be treated in the next paragraph.

§ 117. Time between coagulation and milling.

In former years the coagulum was preferably worked shortly after coagulation. The idea was that a longer delay led to a beginning of decomposition and damaged the rubber. Obviously the purple colour due to surface oxydation played a great part in this notion, as well as the yellow, slimy layer and putrid smell which appear when coagulum, in which too little acetic acid had been used, is kept for some time. The use of bisulphite however opened other ways; the increase in production made it more and more difficult always to work all the coagulum in the afternoon after coagulation, and the high price of acetic acid during the war caused the method of milling on the following day to be generally accepted. Rolling on the morning of the day following the coagulation, that is after approximately 20 hours (which method requires the smallest amount of acetic acid) may now be regarded as the most common in crepe-preparation.

Some estates, with a small production, work the coagulum in the afternoon or evening; some others do the first stage of crepeing in the afternoon, but the rolling thin and smooth on the next morning; but since the objections against keeping the coagulum overnight have been completely overcome by the use of bisulphite, which is indispensable in all cases, there is nothing to recommend such procedures. Of course, central factories, which have to work a very large production, sometimes run all day or even day and night.

In § 107 we have already indicated that it makes a difference in rate of cure whether the coagulum is kept for a shorter or a longer time after coagulation.

The change, that takes place, may be regarded as the beginning of maturation, and the effect is an increase in rate of cure and viscosity when keeping the coagulum overnight. The following figures, averages of a large series of experiments, may be regarded as typical:

	Time of cure	Viscosity
Latex undiluted (appr. 30 %), creped same day	110	27
" " " " next day	98	28
Latex diluted (appr. 15 %), creped same day	121	26
" " " " next day	113	26½

Therefore a decrease in time of cure of about 10 minutes, when postponing the milling until next day. The above figures are normal; in actual practice the difference may vary from 5 to 20 minutes in time of cure, and ½ to 4 units in viscosity, dependent upon several factors, amongst which the composition of the latex, the temperature, and others may be of a certain importance.

Whether the coagulum is simply kept in the serum, covered with a layer of water to shut off the air, or kept overnight in water, does not make any appreciable difference in the properties of the crepe prepared from it.

See O. DE VRIES, Arch. 3 (1920), 354 and 372. Keeping the coagulum for two nights in serum or water gave an increase in rate of cure and viscosity. Compare also § 136 on the action of water on the coagulum in sheet-preparation.

The above figures make it clear that irregularities in the time elapsing between coagulation and milling may lead to appreciable differences in rate of cure, so that the standardisation of this factor is not an indifferent matter, so far as uniformity of product is concerned.

On estates with small productions, which can be worked within a few hours, no important differences occur, and it is only when the regular routine is interrupted by holidays or free days, or when a delay occurs due to a breakdown in the factory, that there is a chance of irregularity. In such cases there are marked deviations in rate of cure and the uniformity of the product is spoilt.

The arrangement of the work in larger factories where the milling of the whole product takes a long time would, however, require special regulations to obtain a very uniform product.

Happily, this factor — beginning of maturation when keeping the coagulum overnight — is not of much importance in actual crepe-preparation on estates, as in nearly all cases bisulphite is used to obtain a good pale colour.

Bisulphite not only makes the colour lighter and more even, but also stabilises the inner properties, because it prevents the above mentioned changes in the coagulum (as discussed in § 48), and thereby tends to maintain uniformity in the product, when the time between coagulation and milling is not strictly standardised.

See O. DE VRIES, Arch. 2 (1918), 74 and 102; *ibid.* 3 (1919), 356 and 372.

Hence, where bisulphite is used, it is not necessary to standardise the time between coagulation and milling so strictly, and no great difference develops if on certain occasions, as before a holiday, one works the coagulum in the afternoon instead of on the following day.

If bisulphite be not used, one must keep a fixed time between coagulation and milling, if one wishes to secure complete uniformity in the inner properties of the rubber.

§ 118. Crepeing the rubber.

Crepeing consists in passing the coagulum between differentially geared grooved rolls, by which a thin uneven sheet is formed. At first this sheet of rubber may have many holes, hence the name crepe; by doubling it, and finishing it between smooth rolls, an even band without holes is produced.

The coagulum during crepeing is washed clean, and the desire to place on the market a dry rubber, as clean as possible, caused the older forms (biscuits, cakes, or thick unsmoked sheets) to be rapidly supplanted by the clear, clean and dry crepes. First applied in 1904, this process was much in vogue in 1908 and later years, but then did not extend as rapidly as the increase of production, and in later years more rubber has been turned out in the form

of smoked sheet than of crepe. The merits of both forms will be compared in Chapter XI.

Description of the first crepeing-machine, displayed in an Exhibition at Kuala Lumpur in 1904, see P. J. BURGESS, Bull. Str. F. M. S. 3 (1904), 315. Further descriptions and criticisms *ibid.* 4 (1905), 223, 226 and 459; Trop. Agric. 24 (1905), 239, 253, 446 and 461.

Influence on the elasticity of the coagulum.

Concerning the behaviour of the coagulum during the milling little is positively known. It is very noticeable that in the beginning the coagulum becomes harder and more compact, due as much to the stream of water on the machines as to the cutting and wringing action of the mills. When most of the serum is pressed or washed out, and the coagulum is mangled further, it becomes somewhat more supple and easy to handle. What changes take place, we do not yet know. So far as they have been studied these changes have no influence on the viscosity of the resultant rubber.

Research on such questions is not easy, because when the rubber is little worked, one has also to reckon with the influence of serum-constituents which are not washed out, and with the influence of slower drying of the thick crepe so obtained; both factors cause a beginning of ripening, and, in themselves, increase the viscosity.

One sometimes finds it stated that more or less severe working of the rubber during milling is still noticeable when the rubber comes to be mixed with other substances in the factory. Rubber which has been much rolled is supposed to be easier to handle and „break down”, while rubber which has been less worked is harder, and not so easy to reduce to a cohesive paste. Definite data concerning this have however not yet been secured and no method has, as yet, been worked out to fix this „easiness to break down” in figures. As stated above, the viscosity of a 1 % solution of the rubber is not affected by the amount of milling, unless the rubber becomes decidedly heated in the mills; but whether the velocity with which the rubber dissolves

in benzene — which property would perhaps be more comparable with the „breaking down” — is influenced by the intensity of milling, has not yet been investigated.

Influence of crepeing on the properties of the rubber.

The process of crepeing always makes a peculiar impression on the spectator. The tearing, twisting, and flattening of a substance which later must undergo great strains and stretching, is at first readily condemned as being too injurious and as decreasing the cohesion and elasticity. But in such judgment two things are forgotten; first the enormous plasticity and elasticity of the still fresh, moist coagulum, which restores itself immediately and wholly; and second, the much more severe treatment of the rubber during vulcanisation, in which process the rubber is completely broken down and reconstructed again.

The facts are that in first quality crepe neither the properties after vulcanisation, nor even the viscosity show any noticeable deterioration due to crepeing as carried out in ordinary estate-practice; one can even go much farther and run the rubber 30 to 70 times through the mills without causing any change in inner properties. This is only true, of course, providing the crepe at the end is worked to a constant thickness, so that drying is equally rapid in all cases.

Whilst the mechanical treatment during crepeing does not alter nor harm the rubber, the washing away of serum-substances, and an eventual beginning of maturation when thick crepe (which dries slowly) is prepared, may have the usual influence on rate of cure and viscosity, due to serum-substances and their decomposition products (see § 64, 107 and 112).

B. J. EATON and J. GRANTHAM (Agric. Bull. F. M. S. 3 (1915), 218) found crepeing from 5 to 25 times to be of no influence on tensile strength and rate of cure, except for a slight decrease in the latter property from excessive working. Further experiments leading to the same conclusions are mentioned in Agric. Bull. F. M. S. 6 (1917), 153; Bull. F. M. S. No. 27 (1918), 197.

Experiments by L. E. CAMPBELL (Bull. Ceyl. No 24 (1915), page 2 and 6; Bull. Imp. Inst. 14 (1916), 533) in which the

coagulum was passed from 7 to even 70 times through the rough rollers, gave exactly similar results, namely no influence on tensile strength and a small decrease in rate of cure from excessive working.

O. DE VRIES (Arch. 1 (1917), 17 and 23) came to the same conclusions; besides tensile strength and rate of cure, the slope and viscosity of the crepe were also found unchanged by increasing the milling in any of the mills. It was only by excessive crepeing on smooth rollers with insufficient water-cooling, that a decrease in viscosity could be observed; this point will be treated further on (page 271).

Contrary results, obtained by CL. BEADLE and H. P. STEVENS, are mentioned by S. MORGAN (Prep. Pl. Rubber, page 90), who holds that extra working is harmful to the rubber. The slight decrease in the properties mentioned (resiliency, elasticity and recovery) would however appear to point only to a slight decrease in rate of cure, whilst figures for tensile strength are not given.

On differences between thin and thick crepe, namely a decrease in rate of cure the thinner the crepe is worked, see B. J. EATON and J. GRANTHAM, Agric. Bull. F. M. S. 3 (1915), 397, and O. DE VRIES, l. c.

From this it follows that, so far as inner properties and uniformity are concerned, one is free, in first grade crepe, to regulate the crepeing so as to secure the best results with the machines at one's disposal. Milling once or twice more or less does no harm; one can safely run through the rolls again a piece of crepe which has not come out satisfactorily. Naturally little milling is to be preferred, but from the point of view of economy of time and machinery; sparing the rubber itself need not form a motive.

The false idea, still so generally accepted in circles which are not familiar with latex and fresh rubber, that milling is harmful, and that much milling should be avoided if anyhow possible, probably generates from experience with the milling of dry, several months old crepe. From the general rules of the chemistry of gels it is however clear — and has been proven for rubber as above indicated — that the wet, fresh coagulum may behave in a totally different manner from dry relatively old rubber; and besides, when remilling dry plantation-rubber in the factory, heat may play a role, which is wholly out of the question

in crepeing the coagulum on estates, during which process a stream of water is used.

About the remilling of dry rubber, some remarks will be made in § 126.

That lower grades of rubber are much more sensitive to crepeing will be treated in § 185.

§ 119. Washing with water.

The preparation of crepe has come in vogue from the necessity of delivering plantation-rubber as clean and dry as possible; and it was known that the manufacturers treat wild or Brazilian rubbers in this way, so as to make them suitable for vulcanisation. In this crepeing process the water serves for cooling as well as for the washing out of serum-constituents, and deserves recommendation from both points of view. The cooling can never do harm, although a slight heating, as we shall see, is not so dangerous as one might suppose; and thanks to the thorough rinsing-out of the serum-substances crepe is much less subject to mouldiness, rustiness, greasiness etc. than sheet.

If, however, one has at one's disposal only water of an inferior quality (containing iron etc.), then it is better to be sparing in the use of water rather than to affect the colour of the crepe, which may take on a rusty or orange tint. Of course, the best of all is to use absolutely clean water.

As already mentioned in § 39 we have several times, in large series of samples of good quality, for instance in the regular control of the output of estates, encountered one sample which showed a low tensile strength, whilst the other properties remained normal. A low tensile strength, combined with a low viscosity, would point to a deterioration of the rubber; but a low tensile strength combined with a normal viscosity strongly points to some mechanical impurity. Sometimes the presence of dirt can be shown microscopically, either after swelling the sample in xylol, or after calcinating it; but in other cases we were not able to find positive proof of the admixture of dirt of some kind. The effect on tensile strength of the fine silt in clayey water, treated in § 39, is not yet cleared up.

Examples of crepe with normal and abnormal tensile strength in series of samples from two estates are:

Estate	Sample	Tensile strength	Standard time of cure	Slope	Viscosity	Ash
I	1	0.84	120	—	28.5	0.31
	1a	1.29	115	36.5	—	—
	2	0.30	120 ?	—	30	0.25
	2a	1.00	110	35	—	—
	3	1.03	120	36.5	33	0.23
	3a	1.34	120	37	—	—
II	September	1.36	95	35.5	23.5	—
	October	0.58	90	—	29	—
	November	1.28	100	35	28	—

In the first series the duplicate samples marked *a* were recreped with luke-warm water, and in all cases show a marked increase in tensile strength. The figures for viscosity and ash are normal.

In the second series, the October-sample showed an abnormal tensile strength (sufficiently proved by repeated tests), which could be traced to pieces of dirt by microscopic examination.

This case is a good example of the use of viscosity determinations; the normal viscosity indicates with certainty that the low tensile strength must be due to some cause foreign to the rubber, the intrinsic strength of which cannot diminish without the viscosity deteriorating also.

With some filters (for instance the Jewell system) alum is used for purifying the water. Alum is harmful to the rubber (see § 88), but the remnant quantity of alum in the water (after it has flocked out the impurities) is usually so small, and therefore so little is absorbed by the rubber, that the effect of it on the inner properties, so far as investigated, is not noticeable.

See O. DE VRIES (Arch. 4 (1920), 178 and 214), who found no influence of water cleared with alum, when it was used to dilute the latex to 15% as well as to wash the rubber during crepeing.

§ 120. The effect of heating during milling.

When cooling with water is not sufficient, the crepe may become warm. In practice it is seldom that this will go far enough to injure the inner properties. First grade crepe must become quite warm before the viscosity is reduced; with still more severe handling, especially with warm water, the rate of cure is decreased, but the heating must go very far indeed before the tensile strength and the slope are changed. Even in crepe which has become quite weak and soft by hot milling, the tensile strength, rate of cure and slope are not very much lowered.

See O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 542 and 557), who in a number of experiments found a treatment of the fresh coagulum or crepe with water of 50° to be of no practical influence; soaking in water of 60° to 80° decreased the rate of cure and viscosity, but left tensile strength and slope unchanged. When crepeing on hot rolls or with hot water, so that the resulting crepe became quite weak, the following differences were found:

	Tensile strength	Standard time of cure	Slope	Viscosity
Ordinary crepe. . . .	1.42	125	37	27
Rolled with hot water.	1.38	140	38 $\frac{1}{2}$	10

Heating the crepe is never desirable and had better be avoided; but one need have no exaggerated fear of it. First quality rubber can very well stand some heating; and such heating as may sometimes occur on estates will probably never be the cause of deterioration of any importance.

With lower grades one must however be more careful, as these deteriorate more quickly on heating (compare § 185). A Universal or some such washing-machine is best for these sorts of rubber.

§ 121. Thickness of the crepe.

The best thickness for crepe is between 1 and 2 mm. Thick crepe dries too slowly; and when the drying takes 3 or 4 weeks instead of one, the crepe becomes noticeably quicker in cure; and, since the drying is naturally greatly dependent upon weather conditions, great variability between the products of different months may ensue. Besides these drawbacks (need of great drying-space, and lack of uniformity in rate of cure) the slow drying often gives rise to spotting, which makes the crepe less attractive in appearance, and may injure the inner properties (see § 168).

Although therefore thick crepe in itself is not of less value than thin — but one would also be on a false track by supposing that it is better than thin crepe, because it is less strongly rolled (see § 119) — in practice the difficulties are too great, and the preparation of thick crepe is not to be recommended.

That crepeing thin may give a slight decrease in rate of cure, by the removal of more serum-substances and the quicker drying, was treated in § 119.

For experiments on preparation of thin and thick crepe see Bull. Ceyl. Nos 23 and 24, and Bull. Imp. Inst. 14 (1916), 515 and 16 (1918), 444. Further S. MORGAN, Prep. Pl. Rubber, page 90.

On the other hand it is not advisable to make the crepe too thin. Thin crepe dries very quickly, but a great deal of space is needed to hang it, and owing to the danger of tearing it can not be hung up in long strips. The greatest difficulty, however, is that the sheets of thin almost membranous crepe stick firmly together, which forms a difficulty in the handling and makes the contents of the chests less sightly. This condition is often wrongly condemned as „damp” or „moist” on the market, though the moisture-content of the rubber may be quite normal, and the fresh somewhat sticky feeling only due to the extreme thinness of the crepe.

The preparation of blankets and such types of thick crepe will be treated in § 126.

§ 122. Machinery.

From the above it will be clear what demands crepe-machines have to satisfy. On the inner properties it makes no difference how the rubber is creped or what machines are used. For economical reasons one ought so to choose the crepeing machines that with as little working as possible a good external appearance and a good thickness is obtained.

Though, of course, a judicious choice of machines is of much importance, and may help to the smooth running of the factory and to the uniformity in exterior of the output, we will not discuss this subject at length in this book, which treats of rubber preparation only in so far as it affects the properties of the product.

§ 123. Keeping of moist crepe.

After milling it is customary to hang the crepe up quickly to dry. There is little reason for letting the crepe lie; keeping it under water, which deserves recommendation in sheet-preparation to soak out some of the serum-substances (see § 139), is, of course, unnecessary with crepe, because of the thorough washing which it has already undergone.

It may however be of interest to point out that crepe still contains so much of the serum-constituents that, by keeping it moist (for instance rolled or folded up), a beginning of maturing may arise, and that after the lapse of some time, say a week, the inner properties are altered in the direction of matured rubber, although the differences remain much smaller than those which we treated in § 108 for coagulum which still holds enclosed a great deal of serum.

The following changes were observed by keeping freshly rolled crepe for one week in closed vessels (O. DE VRIES, Arch. 3 (1919), 341 and 369):

	Tensile strength	Standard time of cure	Slope	Viscosity
Directly hung to dry	1.33	120	37½	34½
Kept moist for 7 days	1.42	95	36	39

Therefore exactly the same changes as by incipient maturation. Similar results were obtained by B. J. EATON (Agric. Bull. F. M. S. 6 (1917), 152).

In addition to the fact that it is better to hang the crepe to dry as quickly as possible, because in this way variations in rate of cure are avoided, this procedure is also strongly to be recommended because on or in the moist crepe (but this only after a few days keeping) moulds and spots may develop (see § 168).

Keeping the freshly rolled crepe under water has naturally less effect than the same treatment of sheet or unmilled coagulum, which contain so much more serum-substances (see § 136 and § 139). Some serum-constituents however are still removed from the crepe; this is noticeable in a small loss of weight (see § 128), but the rate of cure and the viscosity are unchanged by a short soaking, and increase somewhat if one keeps the crepe under water for about 24 hours.

If the soaking lasts longer, for say a week, further ripening goes on; the rate of cure increases markedly, the viscosity increases somewhat, while the slope decreases (becomes better). These are the phenomena of ordinary maturation. The same result is gained by immersing the crepe in serum for some time. The accelerators of vulcanisation that are formed in the wet crepe therefore do not appear to be washed out by soaking in water or in serum.

See O. DE VRIES, Arch. 2 (1918), 225 and 238; *ibid.* 3 (1919), 340 and 369. Soaking freshly rolled crepe in water for some hours was found to have no effect on the properties of the rubber; keeping in water for 24 hours gave a small increase in rate of cure (some 5 %) and no change in viscosity, and this difference became larger by longer treatment. Keeping under water for one week gave the same increase in rate of cure and viscosity and decrease in slope as keeping the moist crepe exposed to the air.

From this it would follow that the soaking of freshly rolled crepe does not lead to an extraction of soluble substances of any practical significance, at least for the inner properties of the rubber: the small loss in weight, to be treated in § 128, indicates that some indifferent substances are extracted. Further the maturation proceeds just in the same way as when the crepe is kept exposed to the air (see page 273);

that is, neither the substances that are decomposed, nor their decomposition-products that accelerate vulcanisation, are extracted to any appreciable extent.

Soaking the fresh crepe in warm water was recommended in former years to render inactive the oxydising enzyme and obtain a white colour. This practice, which is treated in § 140, has been completely dropped since the introduction of bisulphite in crepe-preparation.

§ 124. Drying.

Ordinary thin estate-crepe takes about a week (4 to 10 days) to dry. The original moisture-content of the newly hung up crepe is so low (10 to 20 %, usually 15 %), and the drying goes so fast at first, that, once the crepe is hung up to dry, there is practically no chance of any further maturation.

For figures on the moisture-content and rate of drying of crepe-rubber see B. J. EATON (J. S. Ch. I. 36 (1917), 1218 and Bull. F. M. S. No. 27 (1918), 148); G. S. WHITBY (J. S. Ch. I. 37 (1918), 278 T) and F. C. VAN HEURN (Arch. 2 (1918), 24 and 117). The moisture-content, which shortly after machining was 10—17 %, decreases in 24 hours to 2—7 %.

Variations in the method and rate of drying of the crepe, practically speaking, give no rise to changes in inner properties or to variability in the product. Even in drying sheds with artificial heating the temperature never becomes so high as to be a factor which influences either the properties or the uniformity of the product (see § 125).

Only with very badly located drying-houses, which lie in the dampest instead of the windiest spot of the estate, does one have trouble with too slow drying, and with spotting (see § 168).

Thick crepe gives more trouble in drying. The interior remains moist a long time, slow drying rubber (see § 106) may be formed and the drying may take weeks. This is coupled with changes in which accelerators of vulcanisation are formed. Indeed, with crepe of some 1 cM. thickness one has in reality not to do with crepe but with cake- or slab-

rubber, though perhaps with a rather low content of serum-substances. The making of thick crepe is not to be recommended (see § 121); it is much better, when one does not have good crepeing machines at one's disposal, to make the rubber into sheet. As therefore the drying of ordinary thin crepe has no influence on the inner properties and is not a cause of variability, one can regulate the drying as suits best, and there is no need strictly to standardise the procedure. On this point, as well as in rolling, crepe-preparation is simpler than the making of sheet, where the milling and drying must be standardised to the greatest possible degree, if one wishes to minimise variability in inner qualities.

That the rate of drying is to a considerable extent dependent upon the method of preparation, has already been mentioned several times. The longer the time between coagulation and hanging to dry, the slower the crepe dries (see § 106); keeping the coagulum overnight gives a somewhat slower drying rubber, but the difference is not of much practical importance. Several methods of coagulation give slower drying rubber, for instance coagulation by alcohol, alum, sodium chloride or seawater, sulphurous acid; spontaneous coagulation by different methods also somewhat retards the rate of drying (see § 94—97). Of practical importance is that the use of sodium sulphite as an anti-coagulant, or of sodium bisulphite as an anti-oxydant, retards the rate of drying (see § 44 and 48), whilst addition of formalin to the latex gives a somewhat quicker drying crepe (see § 43 and 106).

On slow and quick drying rubber, and treatments to hasten or to retard drying — which, however, are only of theoretical interest — see § 106, page 236.

§ 125. Drying at elevated temperature; vacuum-drying.

To quicken drying, and to be sure that no spots develop on moist days or on occasions when the drying house is over full, many estates have provided their drying houses with some system of heating flues or of supplying hot air. Generally the temperature reached barely exceeds 40° C, and an influence on the rubber is not to be observed.

B. J. EATON and J. GRANTHAM (*Agric. Bull. F. M. S.* 3 (1915), 443) found no change in rate of cure, but a decrease in tensile strength, by keeping wormed rubber in a hot air drier at 55° C for 1 to 7 hours.

L. E. CAMPBELL (*Bull. Ceyl. No. 24* (1915); *Bull. Imp. Inst.* 14 (1916), 530) found no difference in rate of cure and tensile strength between crepe dried in the air at ordinary temperature or at 50—60°.

In this connexion it is however worth while to discuss what the influence of higher temperatures on the moist and dry crepe may be.

Heat on moist coagulum may have the effect of quickening maturation (see § 108); but as maturation during the drying of crepe is practically excluded by the low moisture-content, this factor does not come into account. In § 145 we shall see that the influence of the temperature of drying is of no practical significance in the drying of sheet; and this is the more so for crepe.

Heating the dry rubber in the air was found without effect for temperatures of 65° C and lower, at least for heating during 5 hours only. Even at 80° C the properties after vulcanisation remained unchanged, and only the viscosity decreased somewhat; and it was only by heating several hours in the air to 90—100° that, besides a marked decrease in viscosity, a deterioration in tensile strength could be observed, whilst rate of cure and slope remained the same.

See O. DE VRIES, *Arch.* 2 (1918), 553 and 560.

F. C. VAN HEURN (*Comm. Delft VI*, page 203) found that heating for some hours to 130° C in an atmosphere of carbon dioxide increased the rate of cure markedly. Heating to 80° C in the air for 1 to 3 hours gave no change in properties.

G. VERNET (*Bull. I. Ch.* 14 (1911), 935; *C. Gp.* 1912, 6143) does not approve of the use of heat in drying rubber, and would prefer drying in the cold, at not more than 28°, with the aid of refrigerators producing dry air (*ibid.* 937 and 6147).

The action of heat on dry rubber, by which it becomes sticky and weak, need therefore not to be accompanied by a change in properties after vulcanisation; and this is readily understood, as during vulcanisation a very much higher temperature is applied. The effect of prolonged heating, say

for several days, at higher temperatures, which would give more ample occasion for oxydation, has not yet been studied in detail.

Rolling dry crepe many times on hot rolls, without water-cooling, may give a decrease in viscosity and tensile strength, whilst rate of cure and slope remain the same (O. DE VRIES, l.c.).

In former years, when much trouble was experienced in crepe-preparation due to spotting during too slow drying, much was expected of quicker drying by heating in vacuo. Since estates have learned to keep the colour of the crepe better by the use of bisulphite, and also to secure rapid drying in the air by rolling thin and well ventilating the drying sheds, the vacuum-apparatus has gone out of use, because it demands regular and expert supervision, besides extra costs in the form of steam or other heating medium; while this method of drying gives extra work since the dry crepe, which has become somewhat weak and sticky, must always be remilled.

A temperature of 50° C (120° F) is usually prescribed. Drying in vacuo at this temperature has little influence on the viscosity and rate of cure of the rubber, while the tensile strength and slope remain entirely unchanged. With higher temperatures the effect on the rubber may be greater, as we have seen above; and vacuum drying is therefore not wholly without danger. Care should always be taken that the temperature does not rise much, nor for long, above 60° C, and regulating this demands careful supervision.

The drying of rubber in vacuo was already proposed in the early years of plantation-rubber; see for instance P. J. BURGESS (Agric. Bull. Str. F. M. S. 4 (1905), 466), who did not recommend its use. For a discussion on its advantages and disadvantages see for instance Lectures 1908, page 75. Manufacturers, who used this method of drying after washing and recrepeing the raw rubber in their factories, were not prejudiced against vacuum drying; but, as mentioned above, the costs and the great need for supervision made this procedure less desirable for use on estates.

B. J. EATON (Agric. Bull. F. M. S. 4 (1916), 219; also Bull. F. M. S. No. 27 (1918), 160) found the rate of cure and tensile strength of thin crepe, in a large series of experiments, to be the same after vacuum-drying as after air-drying.

L. E. CAMPBELL (Bull. Ceyl. No 24 (1915); Bull. Imp. Inst. 14 (1916), 530) arrived at the same conclusion. Though the crepe became sticky and, judging from appearance, would have been declared to be badly over-heated, the mechanical properties had not suffered.

O. DE VRIES (Arch. 2 (1918), 552 and 559) in one case found the rate of cure markedly increased and the viscosity decreased by drying crepe 5 hours in vacuo; heating dry crepe in vacuo gave only a small decrease in tensile strength and viscosity, whilst rate of cure and slope remained the same (l.c. page 553).

§ 126. Recrepeing dry rubber; thick and blanket crepe.

First quality crepe from estates is practically always delivered in a thickness of 1—2 mM.; the lower grades are generally somewhat thicker, say 2—3 mM. It is only when machinery is very insufficient that estates make a crepe of 4 mM. and more, as such crepe dries very slowly and is, in moist periods, very subject to spotting.

The thicker types of crepe, which come to the market, are of the following kinds:

- 1) thin crepe rolled together, to pack more densely;
- 2) blanket from remilled vacuum-dried crepe;
- 3) mixtures of lower grades, scraps of different sorts etc.

In general, the recrepeing of dry rubber has no influence on the inner properties, provided that no appreciable heating takes place. On estates the recrepeing is generally done with water-cooling on the ordinary machines, so that no heating is to be feared; the water is only to a small extent absorbed by the rubber, which after a few days hanging becomes dry again. No soluble substances are extracted, and rate of cure and viscosity remain unchanged; and when the crepe does not become hot, there is no reason for a change in properties in any direction.

See B. J. EATON, J. GRANTHAM and F. W. F. DAY, Bull. F. M. S. No. 27 (1918), 153. Further Bull. Imp. Inst. 16 (1918), 446.

The first of the above named types was prepared on some estates at the time when shipping space was very scarce. Eight layers of crepe were put on the top of each other

and, with a little water, passed four times through the smooth rollers, by which the layers were pressed together. The crepe of 4—5 mM. thickness thus obtained was neatly trimmed into dimensions which exactly fitted the cases, and in this manner the weight of rubber per chest could be augmented by 25 %. Under ordinary circumstances this procedure is however much too expensive, as not only does the recrepeing entail some cost, but especially the trimming gives a large proportion of cuttings, which on remilling give a crepe of somewhat darker colour, which does not fetch the top price.

As was to be expected, the properties of such remilled rubber were found to be exactly the same as of the ordinary crepe from which it was prepared.

The second type, well known as blanket crepe, is obtained from vacuum-dried thin crepe, which has become somewhat sticky and has to be remilled before packing. Several layers are milled together, and the blanket has to be dried in the air.

The same type may be obtained when matured slabs are cut into worms, vacuum-dried and blanketed.

The remilling in this case also produces no change in properties of the rubber.

See B. J. EATON, J. GRANTHAM and F. W. F. DAY, Bull. F. M. S. No. 27 (1918), 161.

The third type is prepared by mixing and milling together dry rubber of very different grades; accidental pieces of good quality, but somewhat lacking in exterior owing to spots, streaks or other irrelevant faults, about which buyers are still so keen, may be mixed with lower grades, small lots of rubber from different origin, misformed sheets, rubber from native planters, and all the scrap of rubber planting in general. Though this procedure must be regarded as very useful for bringing otherwise unsaleable rubber into a marketable form, the properties of the product so obtained may of course vary over a wide range, according to what is put into the mixture.

§ 127. Smoking crepe-rubber.

Smoking the crepe has repeatedly been tried with the idea that smoking ameliorates the quality of the rubber.

This however was found not to be the case, and as the smoked crepe, with its dark brown colour, is classed on the market amongst the brown crepes and paid for accordingly, smoking of crepe is far from profitable and never practised.

The effect of smoking crepe on its quality is not yet wholly cleared up; the results of different investigators are somewhat at variance, evidently owing to the complicated factors that enter into the smoking process (heat, widely differing smoke constituents, etc.).

A very small improvement in quality from smoking crepe for 1—3 weeks was mentioned by S. MORGAN (Prep. Pl. Rubber, page 212).

Extensive experiments by B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 184) however proved that the tensile strength and rate of cure are not changed by smoking the crepe; the average times of cure of the smoked and unsmoked samples were found to be exactly the same.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 499) in one experiment found the smoked crepe to cure much (47 %) slower than the unsmoked crepe, whilst the tensile strength had deteriorated markedly.

§ 128. Differences in weight in the preparation of crepe.

Although a great part of the serum-constituents are washed out in crepe-preparation, different methods of preparation can still give differences in the total weight of market-rubber. We do not mean here the losses through milky serum, of which we spoke in § 115, nor the losses during milling (see § 129), but in the first place the differences in weight due to differences in the content of by-substances in the rubber.

It makes, for instance, a difference whether one coagulates from dilute or undiluted latex. In § 64 we have shown that crepe from undiluted latex cures more quickly and has a higher viscosity, which is probably due to a higher content of non-rubber substances. The ash-content of crepe from undiluted latex is somewhat higher, for example 0.3 % for 30 % latex as opposed to 0.2 % for 15 % latex (see § 64). In conformity with this, crepe from diluted

(15 %) latex weighs $\frac{1}{4}\%$ to $\frac{3}{4}\%$ less than crepe from undiluted latex.

Further it makes a difference whether the crepe is milled a few hours after coagulation, or on the following day; in the first case one obtains about $\frac{1}{2}\%$ more rubber by weight. The explanation of this fact is not yet certain. Probably it has to do with changes in the serum-constituents, which also cause crepe which is milled on the following day to vulcanise more quickly.

If one allows the coagulum to mature for a week in the serum or in the air, then a further decomposition of the non-rubber substances takes place and the loss in weight amounts to 2 % or $2\frac{1}{2}\%$ (see § 108).

If one keeps the coagulum over night in water, instead of rolling it directly or keeping it in the serum — or if one keeps the milled crepe under water for some time — there is also a loss in weight, which according to the manner of treatment may amount to from $\frac{1}{2}\%$ to 1 %.

It is plain that the variations in weight in crepe-preparation are not great. The most generally used methods of preparation give variations in weight of $\frac{1}{2}\%$ or 1 % at the most; only in maturing the rubber a greater loss of weight may occur.

O. DE VRIES and H. J. HËLLENDORRN (Arch. 2 (1918), 396) give the following ratio of weights for crepe prepared in different manner, which figures, of course, are only to be regarded as types, because so much may depend upon the methods actually applied.

1) Crepe from undiluted latex, rolled some hours after coagulation	100.9
2) Crepe from 15 % latex, rolled some hours after coagulation	100.5
3) Crepe from undiluted latex, coagulum kept overnight in the serum and rolled next morning	100.3
4) Crepe from 15 % latex, coagulum kept overnight in the serum and rolled next morning	100.0
5) Crepe from 15 % latex, treated as No. 4, but the freshly rolled crepe soaked some hours in water:	99.8
6) Crepe from 15 % latex, as No. 4, but soaked 24 hours in water	99.6
7) Crepe from 15 % latex, coagulum a few hours after coagulation put in water, and creped next morning	99.7

- 8) As No. 7, fresh crepe soaked in water 24 hours: 99.6
- 9) Crepe from 15 % latex, coagulum kept in the serum for 48 hours and then rolled 99.5
- 10) Crepe from 15 % latex, coagulum kept in the air (matured) for two weeks, then creped . . . 97.5—98

§ 129. Loss of weight in crepeing.

In the preparation of crepe one has commonly, dependent upon the hardness of the coagulum and the type of macerator used, a small loss of rubber due to the flying away of some pieces during milling.

This loss is greatest when the coagulum is hard; for instance when the latex is coagulated in different sheds on the divisions, and the coagulum transported to a central factory. In some cases the floor around the first mill may be white from small pieces of coagulum; but even then the total weight is seldom important, and commonly remains below 0.1 % of the production. Naturally one can catch most of the pieces with a screen in the drain, but crepe made from these remnants has a rather dark colour, and is commonly of inferior quality, because it is often soiled with oil and dirt, so that it cannot be mixed with good rubber.

See O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 364 and 394.

§ 130. The best methods of preparing crepe-rubber.

As a practical summary of the foregoing chapters we may formulate the best methods of preparing crepe-rubber as follows:

- 1) Mix as large quantities of latex as possible in one mixing tank (see § 37 and 55).
- 2) Dilute the latex to a standard rubber-content.

For this one may choose 15, 20, or 25 % dry rubber-content, or use the wholly undiluted latex (see § 69). A content of 15 % gives a softer rubber, which is therefore easier to work and gives less wear on the machines. In the absence of sufficient clean water a standard content of 20 or 25 % is preferable; in which case also a smaller mixing tank is required. If tapping is so regulated that one gets really undiluted latex of

sufficient constant rubber-content, one may also coagulate from this undiluted latex, providing the working of the harder coagulum is not too great a drawback.

- 3) Use $\frac{1}{2}$ to 1 gm of sodium bisulphite per liter of standardised latex, dissolved for instance in part of the water used for bringing to standard dilution (see § 48).
- 4) Coagulate with acetic acid 0.6—1 cc. per liter of standardised latex, added for instance in a 5% solution (see § 83).
- 5) Work the coagulum the day after coagulation.

Working the afternoon after coagulation, which is also sometimes practised, gives a weaker coagulum which is somewhat easier milled, but requires more acetic acid, whilst evening-work in a lighted factory easily gives rise to less careful work and a loss in appearance (see § 117).

- 6) Mill the crepe to a thickness of 1 to 2 mm. (see § 121).
- 7) Dry in the air at ordinary temperature or with slight warming in from 4 to 10 days (see § 124).

§ 131. Points that are of special importance for the properties of crepe-rubber.

After having given in the foregoing paragraph the general lines which have to be followed in the preparation of crepe-rubber, we may draw attention here to some of the points that often occur in ordinary estate-practice and are of special importance for the properties of the product. Practical considerations, which often turn the balance to one side or the other, have been fully dealt with in the respective paragraphs and are generally well known to the practical man; the principal factors affecting the unseen, but very important inner properties of the rubber may here be collected and reviewed.

The following factors have a great influence on the inner properties and should be carefully regulated and controlled.

- 1) Latex from separate groups of trees, fields, or estates usually gives rubber with varying inner properties; therefore one should, so far as possible, mix the latex so as to secure a product of average properties. One should generally not keep the latex from young or

old fields separate, but should mix all the latex which can be brought into one factory or coagulating-place, so that it may all be made into one type of rubber of good average quality.

- 2) The concentration of the latex (dilution in the field or by rain, different rubber-content of different divisions etc.) may give important deviations in properties. Diluting to standard-content is therefore necessary to avoid variability.
- 3) The use of formalin as an anti-coagulant in large quantities is harmful; small doses are allowable.
- 4) The time between coagulation and milling must always be the same. When, however, bisulphite is used, variability from differences in this respect is not much to be feared.
- 5) Thick crepe dries slowly and unevenly, and this, besides giving rise to spotting, may cause variability in the inner properties. Hence thick crepe had better be avoided.

On the other hand in crepe-preparation there are a number of factors, which have little or no influence on the inner properties of the final product, and may therefore be regulated at will or as occasion demands; practical or economic conditions may govern the decision in these respects. Amongst these factors may be quoted the following:

- 1) The quantity of acid, within the usual limits.
- 2) The way the crepe is rolled (number of times and way of rolling).
- 3) The thickness of the crepe, provided it remains between 1 and 2mm.
- 4) The rate and manner of drying (of crepe which is not too thick): in the air, or with artificial heating, with or without mechanical ventilation.

§ 132. Survey of the inner properties of first grade crepe-rubber.

To give an idea of the significance of testing results obtained with our methods we may here mention some figures obtained in the testing of hundreds of samples of first quality plantation-crepe in the Central Rubberstation.

	Tensile strength	Standard time of cure	Slope	Viscosity
1917	1.385	119 ± 8.7	35.9 ⁵	34.5
1918	1.372	118 ± 6.0	35.5	31.0
1919	1.345	110 ± 8.4	36.0	27.2
Average	1.367	115.7 ± 7.7	35.8	30.9

Curves for the figures actually found are given in Chapter XVII; a sufficient idea of the ordinary variations is obtained by placing, beside the above average figures, the following approximate values:

	Average	Normal values	Abnormal values
Tensile strength	1.367	1.35 and higher	1.30 and lower.
Standard time of cure	115.7	110—130	100 and less, 135 and higher.
Slope	35.8	34—38	39 and higher.
Viscosity	30.9	26—43	23 and lower.

It is, however, to be remarked that rubber from young fields, recently taken into the tapping round, generally shows a lower tensile strength and viscosity and a greater rate of cure. Figures such as 1.30 — 1.35 for tensile strength, 20—25 for viscosity and 100—105 for time of cure are in such cases quite normal.

Further it should be taken into account that on most estates in Java crepe is prepared from latex diluted to a certain standard rubber-content, for which 15 and 20% are quite normal. Crepe from undiluted latex, or from latex brought to a higher standard-content, vulcanises somewhat quicker (see § 64), and in such cases times of cure of 95—105 minutes are quite normal.

Further detail-figures will be found in Chapter XVII and in Chapter XI, where a comparison is made between the properties of sheet- and crepe-rubber. We will here only add some data on the ordinary variations of crepe-rubber from one estate, and give some examples of uniform and not very uniform rubber.

The variations in rate of cure and viscosity may be classified as follows :

	Normal	Abnormally large
Variations in time of cure	10—15 minutes	20 minutes and more
Variations in viscosity	7—10 units	15 units and more

An example of the change from a very variable to a uniform product was already given in Fig. 3; here we add two more plates. Fig. 5 gives the stress-strain curves for nine

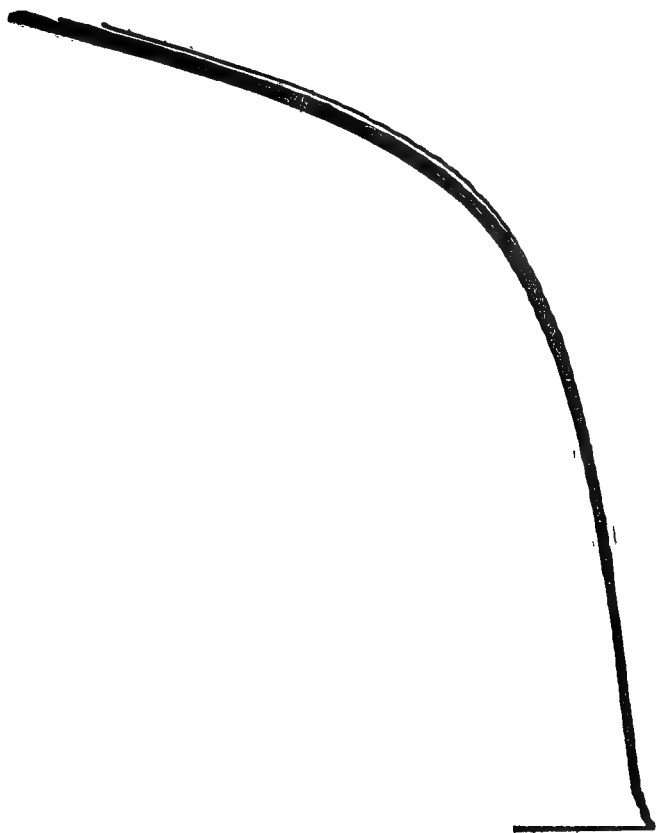


Fig. 5.

Stress-strain curves for samples of crepe from one estate, taken from the output of nine different months, and vulcanised together. Example of an output which is very uniform in rate of cure.

samples of crepe from one estate, taken at random from the production of different months of the year 1916, and vulcanised side by side: the curves nearly coincide, indicating a very uniform product.

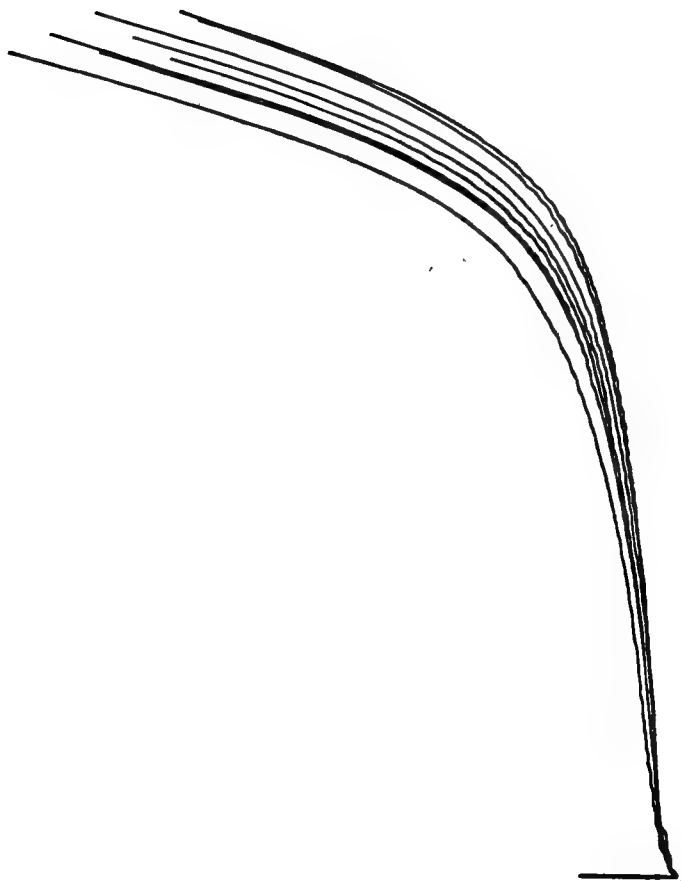


Fig. 6.

Stress-strain curves for samples of crepe from one estate, the output of which was not very uniform in the course of several months (largest difference in rate of cure 20 minutes).

A somewhat larger degree of variation is shown by Fig. 6, where in the same way the product of an estate where preparation is less rigorously standardised is reproduced.

The curves lie rather wide apart; the largest difference in time of cure was 20 minutes.

Figures for monthly samples from an estate producing good uniform rubber are reproduced in the following table; the tensile strength is nearly always normal or good, the rate of cure never differs more than 4 minutes from the average and is very uniform throughout the year; the slope is normal for all samples, and the viscosity is normal, though not high, with normal variations.

Figures for samples of crepe-rubber taken at random from the production of one estate in consecutive months, showing a very uniform product of good quality.

Month	Tensile strength	Standard time of cure	Slope	Viscosity
January	1.36	120	34 ¹ / ₂	30 ¹ / ₂
February	1.44	115	35	35
March	1.37	115	35	31 ¹ / ₂
April	1.36	115	35 ¹ / ₂	26
May	1.41	115	36	33
June	1.42	115	36	31
July	1.35	115	35 ¹ / ₂	33
August	1.36	>115	36	29
September	1.37	>115	36	29
October	1.37	120	35 ¹ / ₂	24
November	1.41	115	34 ¹ / ₂	23
December	1.33	115	34 ¹ / ₂	26 ¹ / ₂
Average	1.38	116	35.4	29.2

CHAPTER X.

PREPARATION OF SHEET-RUBBER.

§ 133. „Even size, even weight, even thickness”.

In the preparation of sheet-rubber irregular lumps or slabs, such as are torn from a large mass of coagulum to be milled into crepe, cannot be used; the coagulum has to be prepared in such a way that a rectangular slab is obtained of dimensions to give a sheet of suitable size for milling, drying and packing. As in sheeting the coagulum is simply rolled thinner, often with only a little pressure in small hand-mills, all irregularities in the original slab, such as differences in thickness or hardness, remain visible in the final sheet, and are often accentuated during drying and smoking.

In the preparation of sheet-rubber it was therefore recognised, sooner than in that of crepe, that strictly standardised methods are necessary. If the latex is not diluted to a fixed rubber-content, if the pans are not daily filled to the same extent with that standardised latex, and if the rolls are not adjusted at the same distance, then sheets are obtained of varying thickness and hardness, which dry with different quickness, and on smoking assume different shades. The different sizes cause trouble in packing, the varying colour necessitates a laborious and expensive sorting. Thus the motto „even size, even weight, even thickness” became generally adopted in the preparation of sheet-rubber, even before it was known to what degree variability in the inner properties is brought about by the lack of fixed rules in the preparation. Only comparatively recent work has taught that in sheet-rubber, besides other factors, the content of serum-constituents and the time between coagulation and drying can cause a great variability in the inner qualities of the product.

These differences are further influenced by many other

factors, such as the thickness and hardness of the sheet, the rate of drying etc., factors which in crepe (of the usual thickness of 1—2 mM.) have, practically speaking, no influence.

The mixing and bringing of the latex to a standard rubber-content was discussed in § 53 and 64—68; the necessity of always filling the pans with the same amount of latex is evident from the foregoing.

§ 134. Form of the coagulating pans.

Latex, for sheet-preparation, is mostly coagulated in smaller or larger pans of different sizes, either of enamelled iron, zinc or wood. Though some types are prevalent, no standard dimensions of pans are generally adopted, and this is comprehensible from the fact that the form of the coagulum has to some degree to be adapted to the width of the mills, the hanging space in the smoke-house, and the dimensions of the packing chests. One of the stages in preparation fixed, all the others would logically have to be adjusted to this once chosen dimension; but a strictly observed relation between dilution of latex, amount of acid used, time between coagulation and milling (that is, hardness of coagulum at the time of milling), amount of latex per pan, dimensions of coagulum, and lastly the dimensions of mills, hanging space and packing material — to ignore other minor points — is seldom adhered to on estates, and the different stages of preparation are mostly arranged in a somewhat haphazard manner, as suits the machinery and materials at hand.

When larger quantities of latex have to be worked, so that the handling of numerous pans would be too complicated, flat tanks of some 15—20 cM. depth are often used, with wooden, glass or aluminium partitions at fixed distances of 1—2 inches, between which the slabs of coagulum are formed on edge, and not lying flat as in the small coagulating pans.

We will here treat these implements only in so far as they may have an influence on the properties of the

rubber. The form of the coagulating pans or the distance between the partitions in the coagulating tanks is not without importance in this respect; as it fixes to a certain extent the form and the thickness of the sheets. If one lets slabs of varying thickness pass through the same set of rolls, then they may (when the rolls are strong) obtain the same, or practically the same thickness, but in that case the thickest slab was pressed heaviest, and therefore dries somewhat more slowly. If one adjusts the rolls at different distances apart, than the thickest original slab remains thickest, and therefore contains more moisture and serum constituents. Both factors—the rate of drying and the content of serum-constituents—can influence the rate of cure; and it depends upon circumstances whether the thicker slab will give a more quickly vulcanising sheet or the reverse.

In fact, differences of 5—15 minutes have sometimes been found in the time of cure of a coagulum from the same quantity of latex, but coagulated in smaller or wider pans, and thus of different thickness. But this does not always occur; for example when the drying both of the thicker and the thinner slabs proceeds very quickly, then no differences arise.

In general, it is desirable, as well for the external appearance as for the uniformity of the inner properties of the product of one estate, to use pans of one size only, and to take care, in tank preparation, that all the slabs of coagulum are equally thick.

For examples of the foregoing points see B. J. EATON (Agric. Bull. F. M. S. 6 (1917), 151, and Bull. F. M. S. No. 27 (1918), 214; further J. S. Ch. I. 36 (1917), 1217 and 1223).

§ 135. Time between coagulation and milling.

In the preparation of sheet-rubber the differences in the time between coagulation and milling may more easily cause variability than in the preparation of crepe.

In the first place with sheet-preparation no use is made of bisulphite, which in crepe prevents differences in rate

of cure from this cause (see § 48 and 117). Using bisulphite in the latex is less desirable in sheet-preparation, because the rubber becomes too pale and dries too slowly.

In the second place, the moisture-content of the sheets, at least at the beginning of the drying, is still sufficiently high for the decomposition-processes (maturation) to go on during the first stage of drying, while in crepe the moisture-content is so low after the milling that practically no more maturing occurs.

Keeping the coagulum after coagulation gives a beginning of maturation (see § 107 and 108) and therefore an increase in rate of cure and a higher viscosity.

Milling on the following day, as opposed to milling a few hours after coagulation, may in the preparation of sheet give a difference of about 5 to 15 minutes in time of cure and of 1—4 units in viscosity.

As a typical example the following average figures may be mentioned:

	From undiluted (ca 32 %) latex		From latex diluted to 15 %	
	Time of cure	Viscosity	Time of cure	Viscosity
Sheets rolled some hours after coagulation.	86	35½	103	33
Sheets rolled next morning (20 hours after coagulation).	76	38	94	36

These differences are therefore not unimportant, and form one of the causes of the greater variability in smoked sheet as compared with crepe.

A strict standardisation of methods in the preparation of sheet is therefore more necessary than in crepe. But in practice this is not always so easy to obtain. It may for instance occur that part of the coagulum must be rolled in the afternoon or evening, and another part on the following morning, due to the fact that there are not enough coagulating pans, so that they have to be used twice or three times

to work up all the latex. Further, holidays or Sundays may cause an irregularity in the routine of the work.

To avoid such differences it is best always to roll the sheets shortly after coagulation. To do this requires a little more acetic acid than when milling on the following day, when the coagulum has more time to set and become hard enough, with a clear serum. But on many estates it is customary to use so much acetic acid that a sufficiently hard coagulum is obtained in a few hours, since by this method the best looking and the most regular sheets are produced.

Rolling the sheets some hours after coagulation has still other advantages, namely that various faults or shortcomings are more or less avoided. Among these we may mention the violet colouration and the formation of spots or patches due to oxydation (see § 107 and 170) and further one of the commonest kinds of airbubbles, which are only formed when the coagulum is milled on the following day (see § 174).

Furthermore, the sheets dry more quickly, the sooner they get into the smoke-house after coagulation.

These reasons make rolling a few hours after coagulation the best procedure in sheet-preparation, and preferable when possible. It has however some drawbacks in practical application. For instance when the latex is rather late in coming to the factory, or when the daily production is too large for all the rubber to be milled in the afternoon (which then often means working in the evening): then one often prefers to postpone the rolling until the following morning, when there is plenty of time, light and supervision.

As has been stated above, a smaller quantity of acetic acid is a further advantage of this last method of working, which is actually employed on many estates.

§ 136. Keeping the coagulum under water.

Whenever it is not possible to roll the coagulum shortly after coagulation, then one has trouble — especially during the time that the latex has a great tendency to oxydation (violet discolouration), such as during wintering or after a

change of the tapping surface — from the violet colouration on the surface of the coagulum and therefore from darker spots on the sheets. Since the use of bisulphite in the latex, which aids so greatly in the preparation of crepe, causes trouble in the sheet — i.e. the sheets become too pale, and the drying goes more slowly — the dose of bisulphite which may be added without drawback (about $\frac{1}{4}$ gm per liter of diluted latex) is not always sufficient, and it is preferable to avoid it altogether. Another way has then to be followed, namely that of excluding the coagulum from the air, so that oxygen has no access and oxydation cannot take place.

This can be effected either by covering the coagulum in the pans with a layer of water or diluted bisulphite-solution (say $\frac{1}{2}$ %), or by taking the coagulum out of the pans and submersing it in water. In using the former method, especially when the latex is diluted to 15 % as is usual in sheet-preparation (see § 68), a drawback is that the coagulum often bulges upwards, so that discolouration occurs on the parts that come into contact with the air; or that the whole mass contracts and loosens itself from the walls of the pan, so that, as it is lighter than the serum, it rises and floats in the liquid. Sometimes this can be avoided by modifying the dilution of the latex; the thinner the latex, the more the coagulum contracts after it has formed, and therefore the more quickly it loosens itself from the pans.

Submersing the slabs of coagulum in water presents the difficulty that a large space is required, since it is impossible to pile the slabs one on the top of the other, because they would stick together; they have to be arranged separately without touching each other.

Coagulating tanks in which the sheets are formed on edge have a great advantage in this respect: discolouration of the edge of the sheets is much less troublesome, just as the settling dirt, which gathers on the under edge, spoils the external appearance of the sheets much less than in the ordinary method of preparation.

All of these different methods of preparation have an influence on the external appearance and the inner properties of the rubber.

Treating the coagulum with water naturally causes it to become harder; besides, serum-constituents are extracted, so that the final weight is decreased and the inner properties altered. When one pours water on the coagulum in the pans the effect is only slight, because it only comes into contact with the upper surface, which moreover is the hardest; but if the coagulum gets afloat, then the water (which then mixes with the serum) may have a stronger effect. If one puts the slab in a vessel with water, then it can effect its soaking action on all sides. So the differences in final weight of the dry sheets, caused by these methods of handling, may vary from nil to 2%.

See O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 70 and 398), and further § 150.

The inner properties sometimes are not noticeably affected, sometimes decidedly so. The tensile strength always remains unaltered, the time of cure can increase somewhat (0—10 minutes), the slope remains unchanged, and the viscosity may decrease somewhat. The changes in the inner properties however, as a rule, are not very large.

O. DE VRIES (Arch. 3 (1919), 358 and 373) found the following average figures in a series of experiments:

	Standard time of cure	Viscosity
Coagulum rolled to sheet a few hours after coagu- lation.	94	39
Coagulum kept overnight in the serum, then rolled to sheet.	90	40
Coagulum immersed in water overnight, then rolled to sheet.	98	38

Therefore the ordinary increase in rate of cure and viscosity by rolling the next morning, but a decrease in rate of cure and viscosity by soaking the coagulum one night in water.

It may be also mentioned here that the keeping of the unrolled coagulum under water is not sufficient to decrease the liability to mouldiness, and does not have the same effect as the keeping of the milled sheets under water. The water rinses the outermost layer of the coagulum, but in the milling and consequent contraction the serum is again pressed from the inner portions of the slab to the surface, and in this way the moulds on the dry sheets again find a rich substratum to grow on.

See O. DE VRIES, Arch. 3 (1919), 346 and 371.

As stated above, all these considerations become superfluous when the coagulum is rolled some hours after coagulation, which, if practicable, is in our opinion the best method of preparation, as we have already discussed in § 135.

§ 137. Rolling the sheets.

The preparation of sheet has, compared with that of crepe, the great advantage that the milling takes less time and requires a less costly installation. Very satisfactory sheets can be obtained even with simple handmills.

But this advantage is, as usual, accompanied by some disadvantages. All the trouble that one experiences in sheet-rubber, in contrast to crepe, in the form of rustiness, greasiness, growth of moulds and such drawbacks, originates in the fact that the serum-constituents are less completely removed from the sheets. Nevertheless, by choosing the right method of preparation, those faults can be avoided; and with adequate care sheets which satisfy all demands can be prepared with only two simple hand-mangles, one smooth and one grooved.

For the uniformity of the product—drying, external and internal properties—it is however imperative always to mangle in precisely the same way, so that the distance between the rolls and the number of times the sheet is milled are once and for all fixed and strictly adhered to. If the latex was properly mixed and diluted, and the pans filled to exactly the same height, then a sheet of the same thickness and hardness is always obtained, which will dry at the same rate, will assume the same colour on smoking and be uniform in inner properties.

Influence on the inner properties.

In § 118 it was stated that the milling to crepe, at least as it is done in estate-practice, is without influence on the inner properties of the rubber; that is to say, as far as the mechanical effect of the milling goes. It will be clear that the milling to sheet, which consists only in a flattening or laminating action by which the material is rolled thin, has absolutely no mechanical influence on the properties of the rubber. Still, in rolling sheet-rubber, more attention is necessary than in crepeing, so that the sheets are regularly rolled and brought to an even thickness, since the thickness regulates the moisture-content and the amount of retained serum-constituents, and also partly the rate of drying, all of which have a decided influence on the inner properties.

It may thus be that sheets from the same latex, milled thinner or thicker, show a difference of 15 or even 25 minutes in time of cure (the thinnest sheet vulcanising the slowest); but in other cases the difference is quite insignificant, and this, of course, depends entirely upon how the drying proceeds, namely, whether or not in the thicker sheets a beginning of maturation really takes place.

For examples of rather large differences in rate of cure in sheets of different thickness, see B. J. EATON, J. GRANTHAM and F. W. F. DAY, Bull. F. M. S. No. 27 (1918), 57.

The sheets are sometimes rolled without water, namely on small vertical hand-mills without water pipes; they are then mostly thrown into a tank with water between the successive millings. On large horizontal mills a stream of water is used, as in crepe-preparation. The treatment of the rolled sheets with water will be discussed in § 139, but it may here be mentioned that milling with or without water usually causes no difference in the properties of the sheets, probably while the serum is pressed out during contraction with some force and removes the water, so that the water washes away some superficial serum, but does not extract serum from the interior during the short moment of milling.

See O. DE VRIES, Arch. 3 (1919), 342 and 370.

Thickness of sheets.

The best thickness for sheet-rubber is 3—4 mM., measured over the ribs. Thinner sheets stretch easier on hand-pulling, which on the market may falsely suggest the idea that they are not so strong; and further they may stretch too much in the first days of drying, when the sheet is still heavily loaded with water, and the thin, rather long sheet gives way somewhat in the parts where it is suspended. Thicker sheets dry too slowly, especially in the thicker parts, for instance the inner parts of the ribs, or an edge or corner which was not fully rolled out to the desired thickness. The interior of such thicker parts may remain moist long enough for the formation of slow drying rubber (see § 106) and it would then take weeks to get such spots dry, even at the temperature of the smoke-house. The practice generally is simply to cut such pieces from the sheets and crepe them.

A thickness of 3—4 mM. permits of a well-pronounced ribbing, whilst the sheets are strong enough to be hung up and, when dry, on hand-pulling offer a good resistance; at the same time the drying is not unnecessarily prolonged.

Rolling.

The number of times that the coagulum is mangled and the way in which the rolls are set can be regulated according to the hardness of the coagulum and the machines which one has at one's disposal.

The external appearance of the sheets is the decisive point; and for the inner properties the manner of rolling is of little importance, provided one adheres strictly to the once chosen methods.

To obtain a well pronounced pattern it is important that the sheets are not too hard and not too thin when they enter the printing machine; clear, outstanding ribs are then obtained, whilst in a hard sheet, especially when it is thin, only a very flat pattern remains when it emerges from between the grooved rolls. With one and the same set of diamond grooved rolls patterns both shallow and deep and of varying form may be obtained, stretched or thick set, dependent upon the conditions chosen.

Generally the coagulum is only passed three or four times through the smooth rolls and once through the finisher with grooved rolls, which prints the pattern and — if one desires it — the name of the estate or company in the sheets.

Machinery.

The machinery used to make sheet-rubber is of still less importance for the inner properties than in the case of crepe. It is only when very weak and badly constructed small hand-mills are used that the coagulum cannot be milled to an even thickness, so that irregularities and variability in the product result, especially when the treatment of the latex and the coagulation are not very strictly standardised, so that differences occur in the hardness of the coagulum to be rolled.

Good results and a uniform product may be obtained with ordinary hand- or machine-driven small rolls; but heavy rolls of 12 or 18 inches diameter have an advantage for the outer appearance, as unevennesses and small faults, such as thick edges, folds and the like are completely obliterated and smoothed out. With smaller rolls, more care is necessary not to offend the tastes and preferences of the market, which, foolish as they may be in the eyes of one who knows the real value and properties of the rubber, have an influence on the price and therefore are of vital importance for the producer.

§ 138. Ribs; plain sheets.

Ribbed sheets are generally made; over smooth or plain sheets they have the following advantages.

- 1) Owing to the increased surface, the drying proceeds quicker and more regularly.
- 2) In packing the sheets do not stick to each other so much, and separation for sampling is easier, while there is less danger of their retaining moisture and becoming mouldy.
- 3) All sorts of faults in the exterior, such as folds or spots, are much more noticeable in plain than in ribbed sheets.

These are the real practical advantages; they are however often overshadowed by the desire to choose such a pattern as gives the best looking outer appearance.

It is in itself evident that the form and dimensions of the ribs only affect the external appearance, and do not in any way influence the inner properties of the sheet. Only indirectly, for instance through differences in thickness of the sheets or an alteration in the rate of drying, the inner properties might be affected, but such differences seem to be small in all cases and as yet have never been determined with certainty. One can therefore strive, to one's heart's desire, to make „lovely” sheets with as beautiful and striking a pattern as possible, at the same time attaining the above mentioned advantages (especially No. 3).

The thickness and the form of the ribs are by no means wholly determined by the form and depth of the grooves in the mangle. As treated in § 137, the thickness and hardness of the coagulum or the sheet, as it enters the rolls, is of at least as much importance.

Instead of a diamond pattern some estates use a striped pattern, consisting of a bundle of small parallel stripes in the length of the sheet, separated by plain bands. The idea was that the water, after milling, would more easily flow down along the vertically hanging stripes, so that no drops remain to dry up in the hollows of the diamonds; in this manner some hoped to prevent rustiness. The fact is that this point has no influence at all on the formation of rustiness, which is caused by slow drying in a moist atmosphere (see § 173), and that the plain bands, being sometimes rather thick, may dry slowly and show all the drawbacks of plain sheet, especially as all irregularities are very visible. The diamond pattern is therefore preferred by most estates, but an interesting point in favour of the stripe- or pyjama-pattern is that more rubber in weight can be packed per chest. Sometimes also the argument is heard that the packed and pressed sheets from the chests are easier separated for sampling.

As a curious instance of what considerations sometimes tip the balance, owing to the present manner of judging rubber on appearance, it may be mentioned that some

estates prefer the stripe-pattern because small air-bubbles (see § 174), when occurring, may be made much smaller or even disappear by passing the dry sheets once more through smooth rolls — a procedure by which the diamond pattern would be too much injured. The air-bubbles which are mostly found in the thickest parts of the sheets (here the plain bands), are pressed away or become less visible, and the market is satisfied and does not depreciate the sheet — though the real intrinsic value of the rubber is, of course, absolutely unchanged.

§ 139. Keeping rolled sheets under water.

An important stage in the preparation of sheet is the soaking of the sheets in water for some time, for instance a few hours or one night, in such a way that the water has access to every part of them. That is to say, the sheets must not be too closely packed together, but must be kept loose and as free as possible, and preferably be stirred or replaced once or twice.

The water dissolves and extracts serum-constituents and especially those on the surface of the sheets, and this is one of the means by which greasiness is avoided (see § 172), and the sheets are made less susceptible to mouldiness (§ 171). In § 136 it was observed that the keeping of the coagulum under water is not sufficiently effective.

It may be mentioned here that soaking the sheets in water does not prevent rustiness; it rather makes the sheets more susceptible to this fault, so that one has to pay more attention that no rustiness can occur, by quickly surface drying the sheets (see § 173).

If the sheets are rolled a few hours after coagulation, then they can be put under water the same day and remain there one night.

If the sheets are rolled the following day, then the procedure of soaking in water can only be less complete: one can leave the sheets in water for some hours, then let them drip for one or two hours, and in the afternoon bring them into the smoke-house. Or one may leave the sheets in water until the following morning, then hang them out, and

after a few hours of dripping take them into the smoke-house. The first method has the advantage that it is all finished in one day, so that the opportunity for the arising of defects (spotting, growth of lower organisms such as moulds in the moist sheet, see § 171) is less, and the rate of drying also is not decreased.

On the other hand it is not yet proved whether the soaking in water for one or more hours (imperfectly as it is done in practice) sufficiently decreases the susceptibility to mouldiness, whilst from the soaking in water for a relatively short time an important decrease in rate of cure is obtained (see below), so that in practice unavoidable small differences in execution of these manipulations give a great chance of variability in rate of cure.

The shorter time in which the product of one day is ready for the smoke-house, the shorter time of drying, and the smaller chance of spotting tip the balance in favour of the former method, and sheets which are rolled the morning after coagulation are mostly put in the smoke-house that same day.

On the colour of the rubber the keeping under water has some effect; generally the colour becomes somewhat lighter and the sheets are very bright, although sometimes indeed a dull colour may develop. The coagulum or freshly rolled sheet is rather susceptible to changes in colour, as we shall see in § 149; and this makes it that the keeping under water may be the cause of darker and lighter spots or patches on the sheet, where the water has free access, or where the sheets stick together or against the wall of the tank.

Spots caused by surface oxydation are described by A. J. ULTÉE (Arch. 4 (1920), A 229) and E. VAN VOLLÉHOVEN (ibid. page A 238); spots of a somewhat different character have been investigated by J. C. HARTJENS (Arch. 4 (1920), 159). The formation of both kinds of spots is furthered by the use of sulphite or bisulphite.

Soaking in water naturally causes a loss in weight, so that by soaking for 24 hours 1—2 % is lost, with longer soaking 2½ %, whilst the loss may even (when keeping under water for a week) amount to 3 %.

See O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 370 and 397.

On the inner properties, especially on the rate of cure, the keeping under water has a very marked effect. Short soaking (for some hours) produces a noticeable decrease in rate of cure and a small decrease in viscosity; if one allows the sheets to remain under water for a longer time (say 24 hours) then the rate of cure and viscosity increase again. Of course the differences may vary very greatly according to the details of the methods; as typical examples the following data may serve:

	Standard time of cure	Viscosity
Sheets hung to dry immediately after milling	93	38
Sheets first kept under water for $\frac{1}{2}$ to 2 hours	109	36
Sheets kept under water for 3 to 5 hours	114 $\frac{1}{2}$	34 $\frac{1}{2}$
" " " " " 20 to 24 "	108	38
" " " " " 44 to 48 "	104	39 $\frac{1}{2}$

Tensile strength and slope remain practically unchanged.

See O. DE VRIES, Arch. 3 (1919), 344 and 370.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 300) found no difference in rate of cure from soaking the sheets overnight, either in running or standing water. This result need not be in contradiction of our above mentioned figures, as the thickness of the sheets, the way of soaking and other details may have caused the rate of cure in one night to return approximately to its former value.

The most probable explanation—for which direct proof, in the form of chemical analysis, has however not yet been adduced—is that short soaking in water gives an appreciable extraction of serum-substances, causing a loss in weight and a decrease in rate of cure and viscosity. By keeping longer in water, more is extracted, and the loss in weight increases; but in the same time maturation processes set

in (which are not hindered by the water, compare § 108 and 136), which cause a further decrease in weight, but make the rate of cure and viscosity increase again, so that the values for unsoaked sheets may be eventually overtaken.

Be this as it may, it will be clear that great differences in inner properties are caused according to whether the freshly rolled sheets are soaked for a short time or not at all; and that this part of the preparation must be carefully standardised if one wants to get a uniform product.

For actual practice a longer soaking (for example overnight) would have preference also in this respect that then it is not necessary to standardise exactly the time and way the sheets are kept under water, as one or two hours more or less gives only a slight difference in rate of cure. At the same time a longer soaking gives the best chance of decreasing the tendency to mouldiness.

It may however be remarked that an effective and reliable method of smoking would be a much more desirable means of preventing mouldiness (see § 146); keeping in water diminishes the weight of market-rubber and may give rise to trouble with spotting, whilst smoking increases the weight somewhat, and covers all differences in colour. It is to be hoped that a careful study of the effective agents in smoking may soon lead to a procedure which with sufficient certainty makes the sheets mould-free, so that soaking in water can be wholly left out, or only done for a short time, to take away the most soluble serum-substances and prevent greasiness.

§ 140. Treating the sheets with hot water.

Several years ago it was the custom on some estates to soak the freshly milled sheets in hot (even almost boiling) water, to prevent rustiness and discolouration by oxydation.

In combating these troubles this method is effective, since it kills the lower organisms that cause rustiness, and puts out of action the oxydising enzymes. It is however not to be recommended, as the properties of the rubber may be greatly harmed. The tensile strength may deteriorate noticeably, the rate of cure is greatly retarded (even 30 minutes or

more), the slope is also affected, and the viscosity decreases markedly. For instance after soaking for 15 minutes the figures may be:

	Tensile strength	Standard time of cure	Slope	Viscosity
Control	1.45	90	36	41
In water of 80° . . .	1.33	125	38	34
In boiling water . . .	1.30	> 120	38	34½

See O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 545 and 557.

The hot water treatment was recommended by M. KELWAY BAMBER to put out of action the oxydising enzymes and obtain a pale rubber (see Lectures 1908, 73; Agric. Bull. Str. F. M. S. 7 (1908), 347, and Trop. Agric. 31 (1908), 300).

Its application on an estate in Java was described by G. VERNET (Bull. I. Ch. 14 (1911), 925; C. Gp. 1912, 5965).

CL. BEADLE and H. P. STEVENS (Rubb. Rec. 1914, 360) mention that the treatment with boiling water weakens the rubber, as it offers less resistance of stretching and is more affected by repeated stretching, which differences may however, at least partly, be explained by the decreased rate of cure.

B. J. EATON (Bull. F. M. S. No. 17 (1912), 32) warns against using this method without thoroughly investigating it first, as it may be supposed to be detrimental to the properties of the rubber.

The hot water treatment had been abandoned in practice and replaced by the use of bisulphite, before its harmful effect was proved by distinct data. Bisulphite is such an excellent and simple means to reach the same end.

§ 141. Hanging the sheets to drip.

The freshly rolled sheets produce a lot of serum which is pressed out by contraction (compare § 106), and continues to flow for some time; the layer of serum on the surface of the sheet slowly drips off, so that it may take from ¼ to 1 hour till the actual dripping has ceased. For the prevention of rustiness it is paramount to

get the sheets surface-dry rather quickly, so that the organisms causing this defect have no time to develop (see § 173). The sheets must therefore be hung wide apart and on a windy, not too cool place; a dark, moist corner of the factory is most unsuitable. After a short dripping time (1—3 hours) the sheets are at once transported into the smoke house.

It should not be forgotten that the fresh sheets in this stage are liable to changes in colour (see § 149), so that different treatment of the surface may result in darker or lighter bands or spots. This is of little importance when the time of dripping is short; but should the sheets be kept overnight, then differences in colour may become very visible, for instance those caused by the sticks on which the sheets hang, or the netting on which they are laid. These darker and lighter spots and patches mostly become practically invisible when the sheets are dry and smoked, just as those formed under water and treated of in § 139; but their appearance may cause some anxiety to the surveyor of the smoke house or the casual visitor.

§ 142. Changes (maturing) in rolled sheets.

While in crepe, on account of its relatively low moisture-content which quickly falls below 10 % after rolling, not much can happen in the way of decomposition or maturation—only a very small acceleration in rate of cure by keeping the moist crepe for a long time (see § 123), and finally the formation of spots (see § 168), and on very wet crepe some mouldiness (see § 168) — sheet, and even thin sheet, contains so much moisture and serum-constituents that precisely the same changes can take place as in the unrolled coagulum (see § 107 and 108).

If one rolls up the freshly milled sheets, so that the moisture does not evaporate, or if the sheets are kept piled on each other, often in a few days one finds just as pronounced a maturation as in coagulum or slabs, and one obtains just as quick a vulcanising rubber. For example:

	Tensile strength	Standard time of cure	Slope	Viscosity
Sheets directly hung to dry	1.45	105	37	34
Sheets left lying on top of each other for seven days	1.47	50	32	58

Therefore the same changes as in ordinary maturation.

Experiments by L. E. CAMPBELL (Bull. Ceyl. Nos. 27 and 35; Bull. Imp. Inst. 14 (1916), 543; *ibid.* 16 (1918), 427 and 449) gave a much increased rate of cure from keeping rolled up fresh sheets; the rate of cure was 120 % to 170 % of the controls, whilst the tensile strength was equally good, and the chemical composition (*ibid.* 16, 436) only changed in so far that the quick curing rubber showed a larger amount of resin and a smaller amount of protein.

B. J. EATON (J. S. Ch. I. 36 (1917), 1217; Agric. Bull. F. M. S. 6 (1917), 147; Bull. F. M. S. No. 27 (1918), 143) found a marked increase in rate of cure from keeping wet sheets, for instance rolled up, and followed the progressive changes in rate of cure in the first eleven days that the sheets were kept wet (Bull. F. M. S. No. 27 (1918), 60).

From this it follows that the method of drying, especially during the first days, may cause great differences in rate of cure. When drying the sheets quickly during the first days, little or no maturation takes place, though such sheets always vulcanise somewhat more quickly than crepe from the same latex (see § 155). If the drying proceeds slowly during the first days—for instance if one allows the sheets to drip for a day or longer, or if the drying-shed or smoke house is very full and poorly ventilated—then the changes by which the accelerators of vulcanisation are formed may proceed a good bit. The rate of drying during the first days is therefore a factor which may cause great variability.

The processes of maturation cease whenever a certain degree of drying is reached. What the limit of moisture-content is, is not yet known; probably it lies between 5 and 10 % (see § 108). Freshly rolled sheets contain some

20—30 % moisture, or even more, and can thus lose a great deal before the maturation ceases owing to a lack of moisture.

On these changes the temperature can also have an influence, since bacterial action usually reaches its maximum intensity at a definite temperature. Thus a temperature of 40° C is mentioned as the most favourable for the phenomena of ripening, while at 60° C the bacteria are a great deal less active. Whenever the circumstances allow it, the higher temperature in the smoke house might therefore promote maturation, and here again is a cause of variability in the rate of cure concerning which exact data are still scarce.

For completeness' sake it may be mentioned that on the outside of the sheets, so long as they are sufficiently moist, bacterial action may take place under formation of a slime or jelly, which results in rustiness, which we will treat further in § 173.

§ 143. Brushing and cleaning the sheets.

On some estates it is customary to brush the freshly rolled sheets as they come from the mills or from the tank with water in which they have been soaked. As long as this is done with water or with a very dilute solution of formalin, no harm results, and in some cases it is useful for the removal of particles of dirt. But in no case can this replace the above indicated methods: soaking in water preferably overnight, and afterwards surface-drying in as short a time as possible. It is true that rustiness can also be avoided by disinfecting the surface of the sheets, for instance by immersing them for a time in a 1 % -solution of formalin; but the air-drying is cheaper and surer.

If the sheets are brushed with too strong a solution of formalin, the rubber will absorb a noticeable quantity of it, and the rate of cure will be retarded, sometimes to such a degree that one gets sheets of wholly abnormal rate of cure.

On other estates the dry sheets are brushed as they come from the smoke house. This method is not bad to remove dirt and dust, eventually also a deposit of tarry constituents, and besides to extract superficially some serum-substances by which the liability to mouldiness is somewhat decreased.

An influence on the properties of the rubber is not to be expected and was never observed.

Even in one case where the sheets, after brushing with water, were laid a short time outside the factory in the sun, no change in properties could be found. But though first quality rubber may stand sunlight better than some suppose, there is no doubt that sunning for a longer time is harmful (see § 164), so that such procedures, being too dangerous in case of neglect or lack of supervision, are not to be recommended.

§ 144. Drying.

After what has been discussed in the foregoing paragraphs it is not necessary to say much more concerning the great influence that slow or rapid drying may have on the inner properties of the rubber.

Fast drying is accomplished by two external factors, namely a high temperature and a low moisture-content of the surrounding atmosphere (obtained, for instance, by a thorough ventilation of the air which has become moist by evaporation). Internal factors however also have an influence. In proportion as the sheets are more porous or harder after rolling, the drying proceeds more quickly or slowly; thin sheets dry quicker than thick ones, because the free surface is in proportion greater; and the method of preparation is also of influence. In general it can be said that the sheets dry more quickly the sooner after coagulation they come into the smoke house. Rolling on the following day instead of after a few hours, and keeping under water, retard the rate of drying somewhat; but with the customary temperature and arrangement of the smoke houses the difference is of no practical importance, so that this need have no influence in the choice of a method of preparation.

It should however be remembered that keeping the coagulum a long time in the moist state produces a rubber which dries very slowly (see § 106) and has therefore to be avoided.

The freshly rolled sheets generally contain some 20 to 30 % of moisture, and sometimes even up to 50 %; how

soon this decreases depends upon a number of factors. Free hanging sheets may dry in the air, at ordinary temperature, in 3 to 4, or even in 2 days; on the other hand a smoke house packed full with moist sheets often only gives a slow drying, and after 8 or 10 days the sheets may not yet have become transparent. In general, however, the bulk of the moisture is given off in at most seven days, but the sheets are kept in the smoke house much longer, to get them thoroughly dry, to smoke them somewhat more, and also to wait till eventual stray patches or sheets have become dry, so that the whole lot can be taken out, weighed, sorted and packed at the same time.

For figures about the loss of moisture in sheets on successive days see B. J. EATON (J. S. Ch. I. 36 (1917), 1218; Bull. F. M. S. No. 27 (1918), 148), F. C. VAN HEURN (Arch. 2 (1918), 31 and 122) and G. S. WHITBY (J. S. Ch. I. 37 (1918), 278 T).

Air-drying of sheets, without the aid of heat, is practically never done on estates, as producing smoked sheet is now the rule (see § 146 and 147). Native rubber-planters however often dry their sheets only in the air (or in the sun), and in the treatment of only a few sheets, when there is plenty of space to hang them, there is nothing against air-drying. For experimental purposes air-drying is even sometimes preferred, as the heating and smoking are not so easily standardised, and introduce a source of deviations which may obscure the results.

§ 145. Influence of heat in drying.

The influence of higher temperatures during drying is rather complicated. In the first place they quicken drying, thereby shortening the period during which the sheets remain moist enough for maturation-processes, so that maturation is restricted by the higher temperature, or completely stopped.

On the other hand, however, an elevated temperature, up to a certain degree, stimulates the action of the micro-organisms causing maturation, so that maturation may proceed quicker during the first days of drying.

Strictly conclusive figures to prove this stimulating influence of higher temperatures in the preparation of sheet have however not yet been given, and the fact is more surmised than known. B. J. EATON (Agric. Bull. F. M. S. 6 (1917), 149; J. S. Ch. I. 36 (1917), 1221) determined the influence of higher temperatures on slab rubber (see § 108).

As long as the sheets are dried rapidly, the temperature at which this is effected has no influence on the inner properties of the rubber, at least if it does not rise too high. Drying at 40° or 50° C gives rubber of unchanged properties; it is only when the temperature rises above 60° C that the rubber shows a somewhat lower viscosity (for example $1\frac{1}{2}$ — $3\frac{1}{2}$ units) and a slower rate of cure (for instance a 5 to 10 minutes longer time). Tensile strength and slope remain unaltered in such cases.

See O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 550 and 559), who found no difference in rate of cure or viscosity between sheets rapidly dried at ordinary temperature, at 40, or at 50–60° C. The sheets in the drying-room were completely dry in 3–5 days; at room temperature drying took 6–8 days. Experiments on estates led to the same result.

B. J. EATON however, in a series of experiments (J. S. Ch. I. 36 (1917), 122; Bull. F. M. S. No. 27 (1918), 182) found an average increase in rate of cure of $17\frac{1}{2}$ minutes or 8% by drying in hot air; the velocity of drying is not given, and may furnish the explanation of the difference from our results.

In practice higher temperatures than 50 or 60° C will never be applied, since by so doing the rubber would become weak, the sheets get sticky and troublesome to handle, whilst the appearance is also injured. The external appearance sets a limit to the temperature at which the sheets can be dried, long before the inner properties are affected to any extent.

On the influence of higher temperatures, such as 80–100° C, on the dry rubber, see § 125. The effect on the rubber of prolonged heating (several days or weeks) in the air to temperatures of 70–100° has not yet been sufficiently investigated, and it is not known at what temperature deterioration and oxydation begin to have an influence under such circumstances.

If the temperature rises above 70° C during the first days, whilst the sheets are still moist, then large bubbles may arise (see § 174).

Too high a temperature when the sheets are dry or almost dry makes them weak and causes them to stretch under the influence of the weight of the rest of the sheet, so that the part where the sheet is suspended gets much thinner than the low hanging parts. Even such heating, by which the physical properties of the raw rubber are altered, need not necessarily cause a difference in the properties after vulcanisation; but the viscosity is mostly affected. In such cases the thicker parts of the sheets, which during drying were the lowest and nearest to the oven, often show a somewhat lower viscosity than the thinner, upper parts. The outer appearance would perhaps make one expect the contrary: the thicker parts retain nearly their original form, the thinner parts look injured and misformed, and would more readily be suspected of deterioration in properties. But then how often are appearances deceitful in judging rubber; and how useful would be the judgment of the man who knows, also in other cases of judging on appearance.

§ 146. Smoking.

The good reputation which Brazilian ball-rubber has enjoyed in the past, and still enjoys in many quarters, has given rise to many theories and opinions concerning its cause, about some of which we will speak further in Chapter XIV. In these theories the smoking played a specially important role. It was not only supposed that smoking improves the quality of the rubber, making it harder and more resistant, but it was further suggested that there were different special constituents in the Brazilian smoke which would have a specific influence. In the first years of rubber cultivation it was even proposed to plant the urucuri-palm in the East, or to import its seeds, so as to be able to produce this very special kind of smoke in the preparation of plantation-sheets. This belief in the beneficent results of smoking was strengthened when the first investigators who

earnestly occupied themselves with research in rubber-preparation strongly recommended smoking (basing their opinion on the then still very incomplete methods of testing), and even went so far as to say: „the longer smoked, the better the rubber.”

See the decided and often enthusiastic recommendations by S. MORGAN, Prep. Pl. Rubber, Chapter VIII and X, pages 111, 169, 170, 212, and in many other places

This standpoint is now completely deserted, and it is well known that smoking sooner injures the properties of the rubber somewhat, in so far as it may retard the rate of cure and brings foreign substances into the rubber which, in certain manufacturing processes, have to be washed out again.

Manufacturers repeatedly uttered the opinion that they did not mind smoking very much, and even preferred unsmoked sheet. See for instance W. A. WILLIAMS, Proc. III^d Congr. 1914, page 134; further I. R. J. 49 (1915), 618.

Still, smoking the sheets is now-a-days generally in use, and that for the following reasons.

The use of smoking.

According to the present state of our knowledge one can see two outstanding advantages in the smoking:

1) it acts as a disinfectant and therefore decreases the susceptibility to moulds; perhaps it may also help somewhat in preventing rustiness;

2) it makes the colour of the sheets more even and uniform, since the quickly arising differences in tint in unsmoked sheet are levelled up or made invisible by it, whilst the spots caused by oxydation (violet discolouration) of the coagulum are more or less made to disappear. In fact, the smoke as a „cloak of charity” covers many irregularities in the exterior.

Both advantages are of great practical value. As to the susceptibility to mouldiness, our knowledge is still deficient (see § 171). It appears that the method of smoking or the composition of the smoke is of great influence, but the best method is not yet known.

A further advantage, the increase in weight from the smoke, is of doubtful value, as this is felt as a „loss on washing” by the manufacturer, and treated by him accordingly (see § 150).

W. A. WILLIAMS (Proc. III^d Congr. 1914, page 134) stated that the North British Rubber Co found a slightly higher loss on washing and a slightly higher resin-content in smoked rubber than in unsmoked, while as regards strength the same results were obtained. See however the remarks in I. R. J. 49 (1915), 453.

Smoking the sheets a certain time will therefore always be beneficial and recommendable; heavy smoking and especially continued smoking after the sheets are already dry would seem of no use, and an economic mistake.

Influence on the inner properties.

It cannot be said that the problem of smoking has already been carefully studied from all sides; on the contrary, our knowledge of details, especially about the influence of different smoke constituents, is still very faulty. But so much is evident that about the supposed favourable influence on the inner properties nothing has been proved with certainty.

On the contrary, from experiments by different investigators it is clear that smoking often retards the rate of cure of the rubber, whilst the mechanical properties remain the same.

Some of the first experiments on smoking sheet-rubber, made at the Singapore Gardens, are described in Agric. Bull. Str. F. M. S. 8 (1909), 569 and 9 (1910), 283; the rubber was very favourably judged, and appeared of excellent strength and good quality. See also Ceyl. R. E. 1906, page 76.

S. MORGAN (Prep. Pl. Rubber, page 212) gives several examples of experiments in which smoking was judged to have improved the quality of the rubber, and regards it certain that there is an improvement in quality with prolonged smoking.

B. J. EATON already in his first experiments (Agric. Bull. F. M. S. 3 (1915), 188) showed that smoking retards the rate of cure by some 25 %, and later gave further material to prove this (Agric. Bull. F. M. S. 6 (1917), 148; J. S. Ch. I. 36 (1917), 1220, and Bull. F. M. S. No. 27 (1918), 170 and 182). The smoked samples showed on the average the same time of cure as

the unsmoked sheets, dried in hot air, while smoked sheet in the majority of cases cured slower than unsmoked, air-dried sheet, which difference became more marked, the thicker the sheets, that is the more maturation could proceed during the first days of air-drying.

PH. SCHIDROWITZ, (Rubber, page 75) holds that smoking increases the strength of the rubber and its resistance to oxydation. He further found (Proc. III^d Congr. 1914, page 140) that unsmoked sheet shows a much greater variability in rate of cure than smoked sheet.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 498; also I. R. J. 51 (1916), 829; see further I. R. J. 48 (1914), 807) found smoked sheet to cure only a little (6%) slower than air-dried sheet, whilst the tensile strength was in the average nearly the same. WHITBY regards the widely accepted view, that smoking markedly improves the quality of the sheet, as fallacious.

H. P. STEVENS however (J. S. Ch. I. 35 (1916), 502; also I. R. J. 51 (1916), 832) found greater differences to be caused by smoking the rubber.

In experiments by L. E. CAMPBELL (Bull. Ceyl. No. 27; Bull. Imp. Inst. 14 (1916), 535 and 552) smoking was found to lengthen the time of cure considerably, the time of cure being for instance 102 minutes against 55 minutes for the unsmoked controls, whilst the tensile strength was better for the unsmoked samples.

As the average of a series of comparable samples from estates the following figures may be given to illustrate the differences as obtained in our method of testing.

Description	Tensile strength	Standard time of cure	Slope	Viscosity
Smoked sheet . .	1.33	99	37.1	33
Unsmoked „ . .	1.33 ⁵	89	37.4 ⁵	36

The tensile strength therefore shows no difference, and the slope is also practically the same. As to the rate of cure and the viscosity, on the average the unsmoked sheets show higher values, but this does not hold for all of the single experiments.

The degree to which smoking retards the rate of cure is therefore found very divergent by different investigators. The explanation is that so many factors enter into the process of smoking which have not yet been analysed.

In the first place there are the different constituents of the smoke, about which little is known and on which absolutely no details are given in the above mentioned investigations. Formaldehyde and phenols, and further tarry substances are known to retard the rate of cure of rubber (see § 43 and 46), but in how far they were present in different experiments is not indicated. Even comparative experiments between smokes from different origin (Hevea wood, other wood, oily or resinous substances) are still completely lacking.

In the second place a comparison of smoked sheets with unsmoked sheets generally is understood to mean: smoking and drying at elevated temperature (say 40—50° C), against air-drying without smoke at ordinary temperature (say 25—30° C). Now this generally includes a difference in rate of drying, therefore a difference in degree of maturation during the first days of drying, as we discussed in § 144. The effect of the smoke itself can only be determined when hot air-drying with or without smoke is compared in such a way that the loss of moisture in both cases runs exactly parallel.

Another method to determine the effect of the smoke is to dry the sheets first without smoke (either at ordinary or at elevated temperature), and then to smoke part of them, and compare that part with the unsmoked part. But then this only gives the effect of smoke on the dry rubber, that is the effect of the absorption of such smoke-constituents as dry rubber takes up. Wet sheets may absorb other constituents from the smoke, and further the smoke may be expected to have a disinfectant action, and so perhaps retard or prohibit maturation processes.

From this it will be clear that much further research will be necessary before the effect of „smoking” on quality is understood in all its details.

Drying the sheets first, at least to a certain degree, and then smoking them, was for instance proposed by G. VERNET (Bull. I. Ch. 14 (1911), 933; also C. Gp. 1912, 6049) and A. J. ULTÉE (in a Planters lecture 1919), and might be a means to regulate the desired disinfecting action of the smoke better, and at the same time have a better regulated rapid hot air-drying, with flues instead of open fires or smoke-pots.

Smoke constituents.

As to the active constituents of the smoke and their influence on the properties of the rubber, very little is yet known, as we already stated above. Tar and creosote, as well as carbonic acid gas and carbon monoxide, formaldehyde and acid vapors (acetic acid etc.) have been considered as the active constituents, but our knowledge, both as to their actual influence on the rubber during smoking and as to their disinfectant action (which of them is the best to prevent mouldiness), is still very deficient. Some points were discussed in § 46 (disinfectants) and § 98 (coagulation with smoke).

§ 147. Smoke houses.

From the standpoint of the inner properties of the rubber little need be said concerning the smoke house, if it is only managed correctly; and the difference between them chiefly lies in practical considerations, such as that one type of smoke house is more expensive than another, or that it dries the sheets more quickly, or that it uses less wood, or that it needs less control, etc. These points, which may be of considerable practical importance, will not be discussed at length in this book, as they bear no direct relationship to the properties of the product. Of course different smoke houses can produce a rubber of somewhat different properties, but these differences generally remain within the normal limits of variation of plantation smoked sheet. And further it cannot be said that one type of smoke house always influences the properties in a certain direction: everything depends upon the manner in which it is handled, for instance the rate of drying, the temperature, the smoking factors, which have all been discussed in the foregoing paragraphs.

It may for instance be that in a Barker smoke house, in which the sheets are smoked rapidly and at a rather high temperature, a rubber of rather low viscosity and a relatively small rate of cure is obtained; but from an ordinary smoke house a rubber can be eventually obtained with a still lower viscosity and smaller rate of cure, when the rubber is strongly heated and heavily smoked in it.

Carefully conducted experiments, in which the different features of some of the more common types of smoke houses are compared, have not yet been published; and it would not be an easy task to analyse the different factors, which come into play, and to obtain results that are free from accidental circumstances.

From the above it however follows that, so far as the quality of the rubber is concerned, there is no preference for one or the other type of smoke house; economic and practical considerations may be decisive in the choice.

§ 148. Unsmoked sheet.

For those who are not very confident of the results of scientific research, and who see a much better criterion in the wishes of the market, it must be a rather striking fact that some estates in Java, which are owned by manufacturers and prepare their rubber directly for the factory, have prepared unsmoked sheets for a considerable period. This may at least be regarded as a proof that smoking is not essential to the quality of the rubber.

As opposed to this stands the fact that other estates, which made unsmoked sheets for the market, have all had to stop this, and have changed over to smoking. The disadvantages of unsmoked sheets (greater susceptibility to mouldiness, irregularity in colour and exterior) have already been discussed in § 146, and are decisive. As a supplement to the data given elsewhere in this book (see § 154 and Chapter XI) we will here add some figures for unsmoked, air-dried sheets from estates which prepared the rubber in this form, and for some time regularly sent us samples for testing:

Estate	Tensile strength	Standard time of cure	Slope	Viscosity
I	1.37—1.45	90—105	37—39	34—47
II	1.36—1.45	90—115	37—39½	28—49

Compared with the average figures for smoked sheet (see § 154):

Tensile strength	Standard time of cure	Slope	Viscosity
1.384	96.3	36.7	31.6

the properties of these unsmoked sheets are therefore practically the same, and there is no reason to suppose either that unsmoked sheet is inferior (as some do, principally judging from the exterior), or that it shows superior qualities.

A superiority for unsmoked, air-dried sheet was claimed from the result of experiments in Ceylon (see Bull. Imp. Inst. 14 (1916), 564).

§ 149. Factors which influence the colour of the sheets.

Unsmoked sheets can exhibit all colours from a very pale yellow to a very blackish brown, and this in connection with the way of handling the coagulum and of the eventual use of chemicals.

While in the preparation of crepe one strives to prevent all discolouration and to keep as far as possible to a very light yellow, in the preparation of sheet the discolouring processes are allowed a wider play, and then, by smoking, all those various tints and shades are brought to a dark brown.

Even in this dark brown, however, there are many nuances, and the colour of smoked sheets from different estates varies greatly; and further the demands of the market are not always the same, so that a special colour has to be aimed at for certain markets. In former years, for instance, a much darker sheet was desired than at present. To fill the demand for a certain colour one has in the first place, of course, a means in the smoking, practising it either for a longer or a shorter time, or using a thin or a thick, tar containing smoke.

Further the moisture-content during drying (or smoking) has an influence; the drier the atmosphere, the brighter the sheets; the more moist the atmosphere, the more oxydation takes place and the darker the sheets become.

This effect makes itself felt very strongly if one lets the sheets hang in a moist atmosphere outside the smoke house after the milling; very dark and dull tints can then arise, and rustiness is generally coupled with rather dark, often dull sheets.

A clear, light colour is promoted by quick drying, while many chemicals (sulphite and bisulphite, also formalin; further large doses of acetic acid and alum) may add to making the colour lighter.

B. J. EATON (Bull. F. M. S. 17 (1912), 36) found that drying in an atmosphere of carbon dioxide gives a light coloured rubber.

Finally, keeping under water, whilst preventing oxydation to a certain extent, keeps the colour brighter, although the tint in many cases becomes somewhat dull.

It may be stated that the temperature in the smoke house also has an influence on the external appearance of the rubber: higher temperatures give a glassy and sparkling appearance, whilst drying and smoking at lower temperatures makes the sheets often exhibit a dull and less lively outer tone.

Between the colour and the inner properties no direct relation exists; but indirectly there may be some connection, since the colour depends to some extent on the method of preparation. But very dark sheets, for instance, may as well vulcanise slower than normal (if they became dark by very heavy smoking), as show rather quick curing capacities (if the sheets took a dark colour because they hung in a damp atmosphere before drying, so that maturation took place to some degree). In the same way a low viscosity can also be met with in bright as well as in dark sheets, etc.

§ 150. Differences in weight in the preparation of sheet.

The method followed in sheet preparation can cause differences in weight of the market-rubber obtained by it

in a larger degree than in the preparation of crepe (see § 128), because the amount of serum-substances contained in the sheets may vary over a large range, whilst also the moisture-content may be higher.

The difference in weight between sheets made from undiluted and from diluted latex may amount to 1 %; also the difference between milling immediately or 24 hours after coagulation is greater than with crepe, and may amount to 1 %, that is to say if the sheets are not soaked in water.

The thickness of the sheets may cause further differences, which may even reach 2 % if the sheets are milled without water and are not soaked after milling.

All such differences, however, become smaller and are partially levelled out if one keeps the sheets under water and by so doing extracts a large part of the serum constituents.

With sheets milled shortly after coagulation a decrease in weight amounting even to 3 % may be caused by soaking in water (for instance for some days); soaking overnight gives a loss of 1—2 %. Sheets milled some 24 hours after coagulation may lose about 1½ % in weight by keeping them one night in water.

The temperature at which drying takes place (provided it remains between 40 and 60° C) gives no differences in weight if the drying always proceeds quickly. If the drying is slow, then at elevated temperature an accelerated maturation may take place, which causes a loss of weight.

See O. DE VRIES and H. J. HELLENDORRN (Arch. 2 (1918), 397), who give the following figures as typical for unsmoked sheets, though, of course, the results obtained may vary from case to case, as the methods employed may have such a large influence.

	Ratio of weight
1. Sheet from undiluted latex, rolled a few hours after coagulation and hung to dry the same day.	102.6
2. Sheet from undiluted latex, rolled a few hours after coagulation, the fresh sheet kept some hours under water and hung to dry the same day	101.2
3. As No. 2, the fresh sheet kept 24 hours under water and hung to dry the next day	100.5

4. From 15% latex, rolled a few hours after coagulation and hung to dry the same day	101.5
5. From 15 % latex, rolled a few hours after coagulation, the fresh sheet kept under water for some hours and hung to dry the same day . .	100.1
6. As No. 5, sheet kept under water for 24 hours and hung to dry on the day following coagulation.	99.5
7. From 15% latex, coagulum put under water a few hours after coagulation and rolled the following day	99.7
8. As No. 7, fresh sheet kept under water for some time	99.4
9. From undiluted latex, coagulum kept in the serum and rolled next day	101.4
10. From 15 % latex, coagulum kept in the serum and rolled next day	100.6
11. As No. 10, fresh sheet kept some hours under water	99.6
12. As No. 10, fresh sheet kept 24 hours under water.	99.4

A special point in the final weight of sheet-rubber is the effect of smoking, which may cause an increase in weight by the absorption of smoke constituents. Sometimes the difference in weight between smoked sheets and sheets dried only by heating is very small, but in other cases it may reach 1 to $1\frac{1}{2}\%$, though normally it will and should not exceed $\frac{1}{2}\%$.

O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 369), found an increase in weight up to 1%.

Further data were given by A. J. ULTÉE in a Planters lecture (1919); the increase in weight by smoking was mostly not much higher than 0.5%, and should not be much larger, or else the sheets become too dark. With thinner sheets, and when using sulphite or bisulphite in the latex, an increase in weight by smoke constituents of 1% was found allowable. The smoke constituents were found back in the determination of loss in weight at 95° (the so-called „moisture-content”) and in the acetone-extract (resin-content).

ULTÉE proposed to call the increase in weight by smoking, that is the content of smoke constituents in the sheets, the smoke-number; this figure may be of importance to fix a degree of smoking which is favourable to the colour and sufficiently

prevents mouldiness without unnecessarily loading the sheets with foreign substances.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F.M.S. No. 27 (1918), 304) mention an increase of 0.5% or more in resin-content (acetone-extract) in the case of heavily smoked sheets.

Though, of course, the obtaining of a large weight of market-rubber is something worth striving after in the eyes of the seller, it would not do to choose from the above the methods of preparation giving the largest increase in weight, and further adding to that weight by heavy smoking. It should not be forgotten that the increased weights are caused partly by moisture, as such sheets are very hygroscopic, and partly by easily soluble serum-substances. Sheets from undiluted latex, rolled shortly after coagulation and directly hung to dry, show a large weight, but are greasy or sticky, very liable to mouldiness, and show a marked loss in weight in washing and drying. Heavy smoking also causes an increase in weight by adding foreign substances to the rubber, and though it may be regarded as legitimate and by no means an adulteration, a part of these foreign substances is washed out when the sheets are creped by the manufacturer. What is an „increase in weight” in the eyes of the planter, constitutes a „loss in weight” in the eyes of the manufacturer, and a proportionate reduction in price may be and often is applied by him.

Moreover, practical considerations, such as prevention of greasiness, stickiness, mouldiness, lead to methods of preparation in which the sheets are duly extracted with water, so that the troublesome serum substances are removed. Present day methods of preparation (see § 152) all tend to keep the content of serum substances, and thus the weight of rubber, low.

A comparison between the weight obtained in sheet- or crepe-preparation is given in § 159.

Direct losses in rubber are small in the preparation of sheet. Except the loss due to milky serum, treated in § 115, one has to think of the films formed on the walls of the coagulating pans, where these have become moistened by the latex by moving them, etc. These films can naturally

not be mixed with the sheets in milling, as they would remain visible as irregular spots in the sheets; sometimes they are added to the scraps, sometimes they are lost in the cleaning of the pans. A loss in weight amounting to 0.2 % of the daily production is not uncommon from this source.

The rolling of sheet-rubber, which is so smooth and even, of course causes no loss of rubber, as may be the case on the first mill in crepe-preparation (§ 129).

§ 151. Crepeing sheet-rubber.

Crepeing of sheet-rubber sometimes takes place on estates. In the first place when the coagulum during rolling is torn by accident or damaged by some other cause, so that no sheet can be obtained from it, it may be milled to crepe, which may be of good appearance, though sometimes not quite pale, as no bisulphite was used in its preparation. The inner properties, of course, are just the same as of first latex crepe.

In the second place, thick edges of sheets which dry slowly (see § 106 and 144) and remain untransparent and moist, whilst the rest of the sheets is quite dry and ready to pack, are sometimes cut off and then creped. This gives a brown crepe, the darker, the more smoking was advanced; this crepe is of just the same quality as smoked sheet, but is often classed by the market with the brown lower grade crepes, so that the procedure is not profitable.

That crepeing smoked sheets does not alter the rate of cure or tensile strength, so that the properties remain practically unchanged, was proved in experiments by S. MORGAN (Prep. Pl. Rubber, page 211), by L. E. CAMPBELL (Bull. Ceyl. No. 23, page 5) and by B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 304). Figures for the loss on washing are however not given, and further proof would be needed whether heavily smoked sheets, which lose part of the smoke-constituents on washing, show a change in rate of cure when creped.

§ 152. Best methods for the preparation of sheet-rubber.

Although the preparation of sheet is not yet so thoroughly known in all details as the preparation of crepe, and

though some important questions still await solution, one can, summarising the principal points from the foregoing chapters, indicate the following methods as the most worthy of recommendation.

1. Mix as great quantities of latex as possible in one mixing tank.
2. Dilute the latex to a standard content, preferably 15 %.
3. Coagulate with acetic acid, 0.8 to 1.2 cc. per liter of diluted latex (added say in a 1 % solution).
4. Always use the same quantity of dilute latex per sheet, and take care that the coagulum is always of the same thickness and form (pans of the same form, filled with equal amounts of diluted latex per pan; distance between the partitions the same, when using tanks).
5. Roll the coagulum a few hours after coagulation.
6. Always roll the same number of times, with the rolls at fixed distances, so that the final thickness of the sheets (measured over the ribs) is 3—4 mm.
7. Keep the freshly rolled sheets under water until the following morning; preferably in running water, or water that is changed some times.
8. Allow the sheets to drip for some hours, hanging them wide apart and in a windy place.
9. Afterwards bring them into the smoke house, and take measures for rapid drying, especially during the first days (thorough ventilation of the smoke house, temperature not too low).
10. Regulate the temperature (and rate of drying) and smoking as evenly as possible.

Whenever one cannot, or will not, mill the sheets a few hours after coagulation, but puts it off until the following day, then points 7 and 8 may be regulated as follows:

Keep the freshly rolled sheets under water or in running water for a few hours, then let them drip in a windy place for an hour or two, and in the afternoon bring them into the smoke house.

§ 153. Points that require special care and attention in the preparation of sheet-rubber.

The preparation of sheet-rubber requires more care and attention than that of crepe. As far as the exterior is concerned, a number of points have been treated in the foregoing paragraphs, or will be discussed in the next chapters. We will here only summarise those factors that have a special influence on the properties or the uniformity of the rubber, and which therefore have to be regulated with care to obtain a good and uniform product. They are:

The mixing of the latex.

Diluting the latex to a standard rubber-content.

The use or not of anti-coagulants can produce marked differences in the inner properties; especially by using large doses of formalin large deviations can be caused.

The thickness and hardness of the coagulum (form of the coagulating pans; degree of dilution of the latex, quantity of acetic acid).

The time between coagulation and working.

Milling the same number of times, and equally thin.

The method of extracting (soaking in water).

The rate of drying, especially during the first days.

The duration and intensity of the smoking.

In the preparation of crepe we were able to enumerate a series of factors which have practically no influence on the inner properties. In the preparation of sheet this is not the case. Although, for instance, the quantity of acetic acid (within the customary limits), as a chemical, has just as little influence on the properties of the sheets as on crepe, still, when the quantity of acid is altered, this has an influence on the properties of the sheets. The hardness of the coagulum at the moment that it is milled will namely be changed, and this makes one obtain a sheet of another thickness and hardness, which will dry at a different rate, so that the rate of cure will be changed.

In the same way the little rolling which is applied in sheet-preparation, mechanically, has no influence on the inner properties of the rubber; but still the milling must

be very well regulated, and at all times be done in precisely the same way, since to do otherwise is to alter the rate of drying, and this again causes a change in the inner properties.

§ 154. Survey of the inner properties of smoked sheet.

Summarising the figures to be given in Chapter XVII we here add a few figures obtained in testing smoked sheet-rubber after our methods, to make comparisons easy and to give a general idea of the average and normal values. Further data will be found in § 201, 202, 203 and 237, and also in Chapter XI.

The yearly average figures, obtained in testing several hundreds of estate-samples of different origin, were:

	Tensile strength	Standard time of cure	Slope	Viscosity
1917	1.405	99 ± 9.8	37.2	35.1
1918	1.377	95 ± 10.2	36.5	31.5
1919	1.370	95 ± 10.4	36.4	28.3
Average	1.384	96.3 ± 10.1	36.7	31.6

Around these average values the different figures group themselves as follows:

	Average	Normal values	Abnormal values
Tensile strength . .	1.384	1.35 and higher	1.30 and lower
Standard time of cure.	96.3	85—105	lower than 75 minutes, higher than 125 "
Slope . . .	36.7	35—39	40 and higher
Viscosity .	31.6	26—43	21 and lower

As with crepe-rubber, it is to be remarked that sheets from young trees, recently taken into tapping, often show a lower tensile strength and viscosity and a greater rate of cure. Figures between 1.30 and 1.35 for tensile strength, and between 20 and 25 for viscosity are quite normal for such rubber, whilst the time of cure may be 75—80 minutes.

The variation in rate of cure and viscosity for samples from one estate may be judged as follows:

	Normal	Abnormally large
Variation in time of cure.	15—20 minutes	30 minutes and more
Variation in viscosity . .	7—12 units	20 units and more

A comparison of the variability between smoked sheet and crepe and a summary of the factors which come into play will be found in § 156. From the facts there mentioned it will be clear that the method of preparation gives more rise to variability in smoked sheet than in crepe; and the actual variability is still enlarged by the fact that the production of many estates in recent years has greatly increased, so that the capacity of the factory and the smoke house were often not sufficient, and changes in the method of working often occurred.

An example as in Fig. 7 for estate A, in which the time of cure shows deviations of 35 minutes and the viscosity of 21 units, is by no means an exception among the estates which regularly send us samples for control-testing.

More regular figures are shown in Fig. 7 for estate B; the time of cure over a period of more than a year varies only over 10 minutes, with a tendency in the course of the year to become somewhat smaller; later on it shows larger deviations and increases rather markedly. The viscosity fluctuates from 27 to 46.

That a good and very uniform product can be obtained by well regulating the preparation and strictly following the standardised method is without doubt; monthly figures for

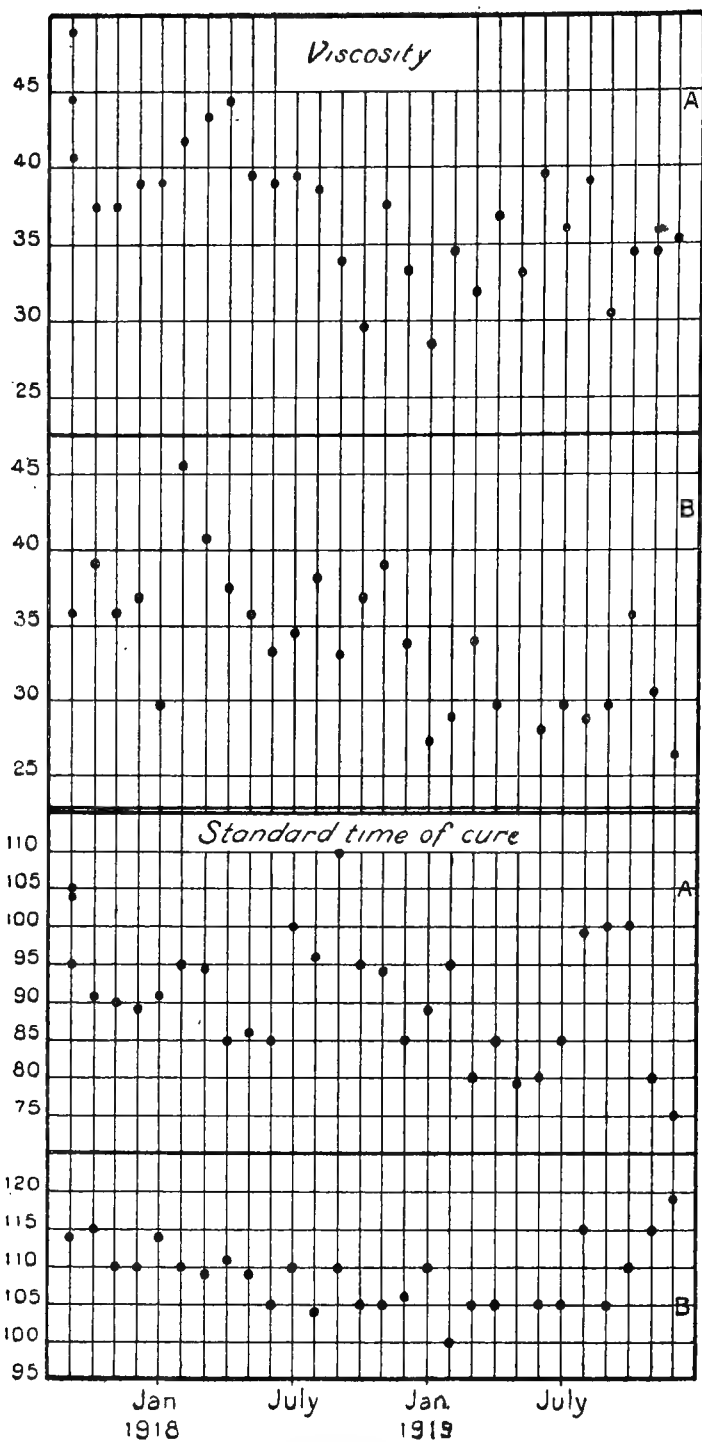


Fig. 7.

Viscosity and time of cure for samples of two estates preparing smoked sheet. A. Large variability in rate of cure because of insufficiently standardised preparation.

B. Output fairly uniform in rate of cure by using standard methods.

another estate, showing a very uniform product of good quality, are given in the following table.

Monthly samples of smoked sheet from the production of one estate.

Month	Tensile strength	Standard time of cure	Slope	Viscosity
January	1.37	80	36	23
February	1.33	85	37	20
March	1.35	85	37.5	21 ¹ / ₂
April	1.26	80	38.5	24 ¹ / ₂
May	1.44	80	37.5	27 ¹ / ₂
June	1.37	80	37.5	35
July	1.48	85	38	30
August	1.26	80	37	26
September	1.27	85	37.5	30 ¹ / ₂
October	1.35	80	36	29
November	1.39	80	36.5	28 ¹ / ₂
December	1.33	80	34.5	24
Average	1.35	82	37.0	26.6

From the two examples in Fig. 7 one sees plainly that the fluctuations in viscosity do not run parallel with those in the time of cure (compare § 235). This is still more to be expected in smoked sheet than in crepe, since (besides other causes, such as differences in the latex, for instance by bringing into tapping young plots etc.) the drying at higher or lower temperatures can give variations in viscosity without altering the rate of cure (compare § 145).

CHAPTER XI.

COMPARISON BETWEEN SMOKED SHEET AND CREPE.

Whether it is preferable to prepare the first latex rubber in the form of smoked sheet or crepe, is a question which depends upon a number of factors, of which we will discuss the principal ones here.

§ 155. Inner properties.

The average figures obtained in the testing of many hundreds of samples from estates, already mentioned in § 132 and § 154, are:

	Average		Ratio	Normal values	
	Smoked sheet	Crepe		Smoked sheet	Crepe
Tensile strength .	1.384	1.367	100 : 98½	1.35 and higher	1.35 and higher
Standard time of cure	96.3	115.7	100 : 120	85—105	110—130
Slope.	36.7	35.8	100 : 97½	35— 39	34—38
Viscosity . . .	31.6	30.9	100 : 97½	26— 43	26—43

These figures hold for estate-samples which arrived for testing from all sides; and though by their very large number they constitute a fairly reliable statistical material, still they cannot be regarded as strictly conclusive for the real differences in properties caused by sheet- or crepe-preparation. It may, for instance, be that most estates newly coming into tapping at first turn to sheet-preparation, whilst crepe comes from a number of old, long established estates. Thus, the influence of young trees, recently taken into tapping, would be greater on the figure for sheet than for crepe.

We therefore add some figures for sheet and crepe, prepared from the same latex, each couple representing the average of several experiments.

		Tensile strength	Standard time of cure	Slope	Viscosity
I. Experiments on an estate . . .	smoked sheet	1.43	90	35½	30½
	crepe	1.39	121	34	27½
II. Yearly production of an estate	smoked sheet	1.34 ⁵	112	36.5	26.0
	crepe	1.33 ⁵	115	35.5	28.3
III. Experiments in the Central Rubberstation .	unsmoked sheet	1.47	82	37.0	29.5
	crepe	1.42	104	37.0	25.7

See O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 388 and 400; O. DE VRIES and W. SPOON, Arch. 3 (1919), 247 and 267.

It will be seen that these differences are of the same order as the average testing results mentioned above.

Comparing the properties as found in our method of testing we therefore have:

1) Smoked sheet shows a somewhat higher tensile strength than crepe.

This difference is however very small, and moreover due, at least for the greater part, to the method of testing. As far as real intrinsic properties go, the tensile strength of the rubber may be accepted as not influenced by the form in which it is prepared (sheet or crepe). The widespread idea that crepeing, as it is done on estates, injures the tensile strength, does not find justification in our investigations and testing-work.

In § 204 it will be discussed at length that the above found small difference in tensile strength in the favour of smoked sheet is due to its greater rate of cure, that is the shorter time it is exposed to the high temperature of vulcanisation.

When preparing sheet and crepe in such a way that they have the same rate of cure, the difference in tensile strength disappears.

2) Smoked sheet has a greater rate of cure than crepe.

This difference, which is caused by a greater content of serum substances and by a larger degree of beginning maturation in sheet-rubber, is rather pronounced in our testing-results and investigations, as both sheet and crepe were mostly prepared from latex diluted to 15 %. If however crepe is prepared from undiluted latex, or latex brought to a high standard content (say 25 %) — a method which is to be recommended, and more and more comes in vogue on estates — then this difference in rate of cure nearly disappears. A time of cure of 90 — 105 minutes is quite normal for crepe from latex with a high rubber-content. The tendency for the difference in rate of cure between crepe and sheet is therefore to become smaller and perhaps gradually to disappear in the course of time.

In how far the present difference of some 5—20 % in rate of cure is an advantage for smoked sheet, which manufacturers are willing to reward by a higher price, is not yet clear.

Several manufacturers have expressed the opinion that a decrease in time of cure of 5—15 minutes (say 5 to 15 %) is of no real advantage to them, and that *uniformity* in rate of cure, be the average 110 or 90, is far more desirable. It should not be forgotten that in many technical mixtures, containing inorganic accelerators, the difference in rate of cure caused by natural accelerators completely disappears.

3) Smoked sheet has a somewhat greater slope than crepe, and is therefore somewhat less resistant to stretching at high elongations.

This is contrary to the still very common conception that smoked sheet constitutes a form of rubber superior in all respects to crepe. The difference, however, is not large, and probably of no practical importance.

To which factor in the preparation of sheet (smoking? drying at elevated temperature?) this increase in slope is due, is

not yet cleared up. The beginning of maturation, which causes the greater rate of cure of sheet-rubber, would decrease the slope somewhat (see § 108).

- 4) The viscosity of smoked sheet and crepe is nearly the same.

Smoked sheet should have a somewhat greater viscosity, coupled with its greater rate of cure, and caused both by the larger content of serum-substances and the beginning of maturation (see § 135). This increase, however, is apparently balanced by the decrease caused by the higher temperatures used in drying (see § 145) and perhaps partly also by the soaking in water (see § 139).

Taken all together, the inner properties of smoked sheet show only a small advantage in rate of cure, which moreover tends to disappear with present methods of preparation; and if there is a real advantage, this is in our opinion more than outweighed by the greater variability of sheet-rubber, to be treated in the next paragraph.

For comparison we here add figures obtained by other workers, by slightly modified methods of testing.

From the experiments made in Ceylon by L. E. CAMPBELL (Bull. Ceyl. No 23, page 4 and 16; Bull. Imp. Inst. 14 (1916), 524) — in which the mixture was 90 rubber and 10 sulphur, the temperature of vulcanisation 148° — the following figures may be compiled.

Description	Tensile strength		Standard time of cure	
	Lbs. per square inch	Ratio	Minutes	Ratio
Unsmoked sheet	2386	100	81	100
Crepe	2286	95	98	121

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 54 (1917), 162 and 184) give figures for the testing of a number of samples from different estates (mixture 100 rubber and 8 sulphur; temperature of vulcanisation 141°). The average figures are:

	Tensile strength		Standard time of cure		Slope	
	Lbs. per square inch	Ratio	Minutes	Ratio	Units	Ratio
Smoked sheet .	1983	100	155½	100	36.2	100
Crepe .	1888	95	182½	117	35.5	98

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F.M.S. No. 27 (1918), 388) give as standard figures:

	Tensile strength		Standard time of cure	
	KG per m ²	Ratio	Minutes	Ratio
Smoked sheet . . .	1.46	100	165	100
Unsmoked sheet . .	1.52	104	135	82
Thin pale crepe . .	1.30	89	195	118

The testing in this case was done in a mixture of 90 rubber and 10 sulphur, vulcanised at 140° C.

The ratio of times of cure is in close agreement from all four testing stations; in tensile strength it is only in the last case that a noticeable difference is found to the detriment of crepe, which EATON repeatedly (for instance l.c. page 81 and 163; Agric. Bull. F. M. S. 5 (1917), 185 and 377) draws attention to as a distinct disadvantage and inferiority of crepe-rubber. We hold the opinion that crepeing does not cause a deterioration in tensile strength (compare § 118 and the discussion above). EATON's figures find no support in the investigations of others, and it remains to be seen in how far this difference is due to some special feature in EATON's testing method, more than to any inferiority in intrinsic strength of crepe-rubber.

An ardent plea for the superiority of smoked sheet above all other grades was given by S. MORGAN, based on the testing results of CL. BEADLE and H. P. STEVENS (Prep. Pl. Rubber, page 185—188, 193 etc.). The following standard figures are given:

	Resiliency	Resistance to stretching	Recovery
Smoked sheet . . .	65.5	140.0	94.1
Pale crepe . . .	58.5	124.0	90.8

showing higher figures throughout for sheet. As however the method employed in this testing does not give figures independent of rate of cure, the principal conclusion to be drawn from the above is that smoked sheet in general vulcanises quicker than crepe, in accordance with what other investigators found. In how far this greater rate of cure constitutes a real superiority, still remains to be seen (see above sub 2, page 334)

The enthusiasm for smoked sheet, based on the above named testing-results, seems at least somewhat exaggerated.

§ 156. Uniformity in inner properties.

In the foregoing paragraph we have already remarked that there is no reason to suppose that the differences in the method of preparation between sheet- or crepe-rubber should affect the *tensile strength* of the product, which — as we will further discuss in § 201 — depends upon deeper going influences, directly connected with the caoutchouc itself, and for first grade rubber principally upon the condition of the trees themselves and the type of caoutchouc they produce. There is, consequently, no reason at all to suppose a difference in variability in tensile strength between sheet and crepe, and the curves given in § 201 confirm this conclusion.

The *slope* seems to be affected to a slight degree by the method of preparation, as it is in the average somewhat higher for sheet than for crepe; but the variations shown by the curves in § 202 are practically the same for both types of rubber.

Comparing the curves for *time of cure* given in Fig. 17 (§ 203) it is clearly seen that the variations for sheet are much greater than those for crepe. In other words: smoked sheet, taken as a whole, as plantations now-a-days produce it, is a less uniform product than first quality crepe.

After what we said in § 131 and 153 nothing else was to be expected; sheet-preparation gives more occasion for variability in the product than crepe-preparation.

In crepe-preparation the use of bisulphite in the latex practically prevents maturation during the time between coagulation and rolling; the coagulum, by rolling, is at once brought to such a low moisture-content that no further changes take place during drying. Eventual variability in crepe-rubber is therefore principally due to the composition of the latex itself and to the dilution (standard content) to which it is brought.

In sheet-preparation, on the contrary, nearly all stages may give rise to variability, unless they are very strictly standardised. So:

- 1) the time between coagulation and rolling (see § 135);
- 2) the thickness of the sheets (see § 137);
- 3) the extent to which they are extracted with water (see § 139);
- 4) the rate and temperature of drying (see § 144—145);
- 5) the smoking (see § 146);

For the 1459 samples from estates, mentioned in § 132 and 154, the figures are:

Description	Standard time of cure	Average deviation in % of time of cure
Smoked sheet	96.3 ± 10.1	10.5
Crepe	115.7 ± 7.7	6.7

The average deviation used in these tables is the sum of the deviations of each sample from the mean, totalled without regard to plus or minus, and divided by the number of samples,

$$\text{or } \frac{\sum d}{n}.$$

As a further proof the following figures may serve, giving the averages of the samples received during a period of 2½ years from 10 estates which prepare smoked sheet, and 10 estates which prepare crepe:

Description	Standard time of cure	Average deviation in % of time of cure	Viscosity, Average	Average deviation in %
Smoked sheet	101.8 \pm 7.17	7.05	32.4	2.8
Crepe	119.4 \pm 5.48	4.6	34.5	3.7

See O. DE VRIES and W. SPOON, Arch. 3 (1919), 254 and 270.

The deviation in rate of cure for sheet is therefore more than $1\frac{1}{2}$ times as great as for crepe.

More strictly conclusive perhaps are the figures for monthly samples from one estate, which regularly prepares both crepe and smoked sheet from the same latex and with equal care:

Description	Standard time of cure	Average deviation in % of time of cure	Limits of time of cure
Smoked sheet	112 \pm 9	8.0	95—125
Crepe	115 \pm 3.5	3.0	110—120

From these figures it may be concluded that smoked sheet generally shows a larger variability than first quality crepe; the average deviation is some $1\frac{1}{2}$ to 2 times as great, so that undoubtedly crepe is the more uniform type of rubber, as might be expected from what we said about the factors in preparation affecting variability in Chapters IX and X.

This, of course, does not say that with adequate care a very uniform sheet-rubber cannot be prepared: we gave an example of an estate turning out smoked sheet very uniform in rate of cure on page 331. But the peculiarities of sheet-preparation are such that differences or changes, which have a marked influence on rate of cure, easily occur; and with the care that can be given to it in ordinary factory-practice, a very strict standardisation of sheet-

preparation, which moreover has to be kept constantly the same over a long period, is only very seldom met with.

Sufficiently large statistical material from other sources, to allow of calculations on variability, is still scarce. From the data published by PH. SCHIDROWITZ and H. A. GOLDSBROUGH (samples from 7 estates preparing smoked sheet and crepe, see I. R. J. 54 (1917), 162 and 184), we calculate the following deviations:

Description	Number of samples	Standard time of cure	Average deviation in %
Smoked sheet	147	155.4 \pm 14.3	9.2
Crepe	132	188.1 \pm 18.3 ⁵	9.7 ⁵

therefore the same degree of variability in sheet as in crepe.

§ 157. Chemical composition.

Data about the chemical composition of smoked sheet and crepe from different origin are still rather scarce. The following figures may however serve to give a general idea.

Description	Moisture-content	Acetone-extract	Nitrogen	Ash	Acidity
Smoked sheet	0.61	2.89	0.45	0.38	0.5
Crepe	0.42	2.88	0.45	0.30	0.1

See Comm. Delft II, page 40–68. About the determination of „acidity” see § 244.

O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 400) found the following average figures for smoked sheet and crepe from the same latex, in a series of experiments on an estate

Description	Moisture-content	Acetone-extract	Ash
Smoked sheet	0.73 %	2.50 %	0.24 ⁵ %
Crepe	0.57 %	2.72 %	0.17 %

The higher moisture-content and ash of smoked sheet (to which may be added the higher water-extract, about which not sufficient figures are available, but which is probably partly due to serum substances, partly to smoke-constituents) make themselves felt in a greater loss on washing and crepeing, about which however sufficient figures are not at hand. Besides this difference, the chemical composition of both grades is practically the same and does not seem to be of any importance in a choice between the two.

§ 158. Other properties; exterior and faults.

Besides the properties after vulcanisation and the uniformity of the product, treated above, there may be other points in which sheet and crepe show differences which cause manufacturers to show a preference for one or the other grade. For instance one finds it sometimes mentioned that the ease of breaking down and the plasticity of sheet and crepe on the mixing rolls is different, so that for some compounds sheet, for others crepe is preferred. Methods of testing which allow a strict comparison on such points have however not yet been made known, so that it is not yet possible to trace such differences to a certain stage in the method of preparation, or investigate whether they are accidental or inherent to sheeting and crepeing.

One of the properties which it is easier to define is the colour; the pale colour of crepe makes this form of rubber especially fit for colourless or transparent articles, for which the dark sheet-rubber cannot be used.

A further point of interest is the faults in the exterior appearance of the rubber, which give the planter more trouble in sheet- than in crepe-preparation. Rustiness, greasiness, mouldiness, faults in the degree of smoking, air-bubbles, are all of them faults which can be avoided by a well-chosen method of sheet-preparation, but which nevertheless cause the planting community a lot of trouble and give buyers occasion to claim many a rebate in price. In crepe-preparation, once the factory is installed, all goes much easier; crepe is not susceptible to rustiness, greasiness, mouldiness, air-bubbles etc., and the only trouble of practical

importance is coloured spots due to slow drying or to chests which become moist during transport or keeping. The practical position is that sheet-preparation requires more care and supervision, and more readily leads to trouble and worry of some kind, whilst a crepe-factory leaves the manager free to give more of his attention to other points; and this, coupled with minor causes, is perhaps the principal reason why certain estates, which started with sheet-preparation, definitely settle on a crepe-factory.

The trouble with moulds and the slow drying of the older thick forms of rubber (biscuits etc.) gave crepe-preparation such a good chance when it was first introduced; see for instance Ceyl. R. E. 1906, page 76, 78, 92 and 114.

§ 159. Differences in weight.

A supposed difference in weight of market-rubber in the favour of smoked sheet played rather an important role some years ago in the choice between the two; figures of 3 to 4 % were given, and an average of at least $1\frac{1}{2}$ % more for sheet-rubber was generally accepted.

See S. MORGAN, (Prep. Pl. Rubber, pages 193–198) who holds the difference to be at least 1 % in favour of sheet, and mentions figures of 3 and 4 %. Whether the experiments, on which these figures are based, were accurate and extensive enough to furnish reliable data on the rather small differences in question, is not clear from the description.

It may be that older methods of preparation gave a larger difference in favour of smoked sheet than is found at present. We think, for instance, of the increase in weight from the heavier and more prolonged smoking in former years, when very dark, thoroughly smoked sheets were demanded by the market; and we think further of the loss in weight caused by the soaking of the freshly rolled sheets in water, to prevent greasiness and diminish the liability to mouldiness, which is now-a-days more generally in use than some years ago.

Be this as it may, with present methods of preparation the difference is certainly much smaller, and only between nil and $1\frac{1}{2}$ % in favour of smoked sheet. On the average

it may be taken to lie between 0.5 and 1 %, with a tendency to become smaller in years to come, by probable changes in methods of preparation (such as preparing the crepe from latex with a high rubber-content, soaking the sheets thoroughly in water etc.)

O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 375 and 396) give the following figures as type for the methods of preparation most generally in use:

	Ratio
Crepe from undiluted latex, rolled some hours after coagulation	100.9
Crepe from undiluted latex, rolled one day after coagulation	100.3
Crepe from 15 % latex, rolled one day after coagulation	100.0
Unsmoked sheet from 15 % latex, rolled in the afternoon and soaked in water overnight . . .	100.5
Unsmoked sheet from 15 % latex, rolled the next day and soaked in water for some hours	99.5

to which figures must be added the increase in weight by smoking the sheets, perhaps 0.5 to 1 %. The difference in favour of smoked sheet would therefore be 0 to 1.5 %.

In a series of well-controlled experiments on an estate, the same authors (Arch. 2 (1918), 387 and 400) found differences of 0.25, 0.20 and 0.54 %, in the average 0.33 %, in the favour of smoked sheet.

A. J. ULTÉE, in a Planters lecture (1919), mentions the following differences in favour of smoked sheet, found in accurate experiments on estates: 0.0, 0.1, 0.3, 0.5, 1.6 and 1.6 %, or on the average 0.7 %.

§ 160. Preparation.

As far as chemicals go, the two forms do not show much difference. For crepe-preparation bisulphite is needed; but then, in sheet-preparation, the dose of acetic acid is generally taken somewhat larger, so that a smooth, well formed coagulum is formed in a short time, which gives the best guarantee that good looking sheets will be obtained on rolling. Although the costs for chemicals would be somewhat higher for crepe, when they are used very sparingly in both cases, still in actual practice the difference is mostly very small or nil.

The coagulating apparatus (tanks or pans) is more expensive for sheet, and more coolies are needed to handle the rubber in its different stages before and after milling. On the other hand, the machinery and number of rolls must be greater for crepe, and the capital outlay for a crepe-factory is always much larger. The fact that two simple handmills are sufficient to produce a very satisfactory crop in the form of sheet, is often—provided that the lower grades can be worked somewhere else in good mills—the deciding factor to start with sheet-preparation, or to work the coagulum to sheet on outlying or scattered divisions.

An advantage of sheet-preparation, that is appreciated by many managers and factory-assistants, is that the rolling takes less time, so that the work in the factory is finished at an earlier hour.

On the other hand a serious drawback is often the scarcity or dearth of wood for the smoke houses, as soon as the plantation is so far thinned out that little Hevea-wood is obtainable from the fields.

Another circumstance which may lead to the choice of crepe-rubber, is when the latex has a strong tendency to premature coagulation or curdling. Sheet-preparation is in such cases often difficult and gives too much off-quality product, whilst a very satisfactory crepe may be obtained.

§ 161. Costprice.

Besides the properties and weight of the rubber, and the above discussed practical considerations, a most important roll in the choice between sheet and crepe is, of course, played by the comparative costs. We will treat some of the principal points here, but of course only in quite a general manner, as details in the matter of prices are of such local and accidental character.

The capital outlay, especially for engines and crepeing machines, is greater for a crepe-factory, and even taking into account the smoking sheds and the more elaborate coagulating utensils needed for sheet-preparation, and comparing a well-equipped sheet-factory with a similar crepe installation, the difference is in the favour of sheet. This

capital outlay weighs on the costs in the form of interest, depreciation, insurance and upkeep; the difference is, of course, dependent upon the type of factory, but may be taken, as an example, at 1 ct per K.G. rubber, or 0.09 penny per lb.

The factory-costs do not show a great difference; chemicals, oil and engine-fuel are higher for crepe, but fire-wood and coolie-charges are higher for sheet. The longer time of working is to the disadvantage of crepe, and perhaps the salary of the engine-driver also. In general (dependent upon the price of fire-wood) the costs are equal, or somewhat to the disadvantage of sheet.

The costs of insurance of the stock are generally higher for sheet, as the product takes $1\frac{1}{2}$ to 2 times as long before it is packed and shipped, so that the stock is larger; and further because the premium is sometimes higher owing to the danger of conflagrations in smoke houses. But this is only a small item in the cost-price.

The packing charges are in favour of sheet, as more weight of rubber is packed in one chest. Assuming that 33 % more in weight of sheet-rubber can be packed in one chest than of crepe, the difference may be some 1 ct per K.G. of rubber (0.09 penny per lb.), dependent upon the price and type of packing cases used.

Taken all together, sheet-rubber will cost some 2 cts per K.G. (0.2 ct per lb.) less than crepe, up to delivery from the estate.

This advantage is increased by the larger weight obtained in sheet-preparation, which may be taken at some 0.5—1% (see § 159), so that the above figure increases to 3— $4\frac{1}{2}$ cts per K.G. (0.3 — 0.4 penny per lb.).

This advantage for sheet-rubber is still further increased by the freight, in so far as it is calculated by volume and not by weight. The transport from the estate is mostly paid per chest, but of course not the volume but the weight of the chest will decide to some degree the price per chest. Railway charges are generally calculated by weight, but shipping charges by volume, and this item may appreciably increase the advantage for sheet before it arrives in Europe or America.

From the above it will be clear that the market-price in the East would have to be some 5 cts per K.G. ($\frac{1}{2}$ penny per lb.), and in Europe perhaps even nearer to 10 cts per K.G. (one penny per lb.) in favour of crepe, to establish an equilibrium between both forms. As the premium for crepe is not always so high, this form of rubber would be doomed to disappear from the market, were it not that other arguments—principally difficulties with fire-wood, and faults in the exterior of the sheets with the accompanying rebates in market-price, which may often reach 2—4 cts per K.G.—sometimes even turn the scale to the other side.

§ 162. Summary.

The deciding factor on which estates choose between sheet- and crepe-preparation is, finally, the profit made by it, all circumstances taken into consideration. The cost-price is the one side, and this, as we saw in the foregoing paragraph, is on the estate slightly to the advantage of sheet, and decidedly so when the shipping freight is included.

The other side is formed by the market-price. The idea has a certain persistency that the price paid on the market is the best and purest criterion to judge of the quality of the product; but it is now fairly generally recognised that this is by no means the case, and that many complicated factors, all together forming the so-called market position of the article, have at least as much influence on the market-price as the intrinsic value of the article in the eyes of the consumer.

When—as has many times been the case in later years—the market-price of crepe is somewhat above that of sheet, then an equilibrium between both forms is reached, and one sees estates starting on sheet-preparation, but others going over to crepe, as the arguments treated in the foregoing paragraphs may lead them.

Since the once supposed absolute superiority in inner properties of smoked sheet is no more a leading motive, and since it is clear that crepe also may be preferred by manufacturers in many cases, so that a demand for it may

always be expected, arguments such as difficulties with firewood, disappointment or trouble with faults in the finished product, tendency to pre-coagulation in the latex etc. often prompt the decision in the favour of crepe, whilst the smaller capital outlay for machinery, together with the difference in packing charges and freight, may turn the scale in the favour of sheet.

For those, however, who are in a position to do so, the best policy is to prepare the rubber in both forms, be it in one large factory or on different estates of one group.

CHAPTER XII.

KEEPING QUALITIES, DETERIORATION AND FAULTS IN THE FINISHED PRODUCT.

§ 163. Changes in properties on keeping the rubber.

Most plantation-rubber, as such, has only a short existence; between harvest and vulcanisation in the rubber-factory, as a rule, not more than a few years elapse, and little is heard of serious deterioration during that time. The general conclusion may be that first grade plantation-rubber stands keeping for some years very well; yet there is no doubt that even excellent rubber may completely deteriorate in the course of years. We examined, for instance, a piece of smoked sheet which had been awarded a first prize at the London Rubber Exhibition of 1911, but which, after seven years keeping in the tropics, had become absolutely brittle and weak by 1918, with a viscosity of only 3 units, while vulcanisation gave a spongy mass and not a satisfactory vulcanisate.

In actual practice the changes which take place in the product during the first two or three years are the most important. Since the investigations on such points are ipso facto a lengthy performance, the information as yet to hand is still incomplete; and on many important points (for instance the difference between keeping in subdued light or in the dark, in a wet or a dry atmosphere, at tropical or European temperatures) no accurate data are as yet available.

From our experience with hundreds of samples, kept at a fairly regular temperature of 27°C in cupboards, we may state that under such circumstances the rubber does not show appreciable deterioration in appearance. The very light colour of pale crepe becomes decidedly darker in all cases, but no other visible change occurs, provided the

samples remain dry enough so that no mouldiness or spots appear; these faults will be treated in the next paragraphs.

As for the inner properties, the *tensile strength* may in many cases remain constant for periods of at least four years. We retested many samples which after three to four years keeping showed the same excellent tensile strength as when tested a few weeks after preparation. Other samples, however, show a gradual decrease, say from 1.40 to 1.30 or 1.20; no apparent reason has as yet been discovered as to why ordinarily prepared samples should in some cases remain constant in properties, and in others show a slow deterioration.

The *time of cure* in a number of cases showed a decrease of some 5 or 10 minutes on keeping, but in others remained constant or increased. The causes of such changes are not yet sufficiently cleared up and need further investigation; from a preliminary review of data it would seem as if in cases where the rate of cure was retarded by some cause or other a decrease in time of cure gradually sets in, whilst rapid curing rubber often showed an increase, so that in both cases the rate of cure, on keeping, gradually returned to more normal values.

The *slope* generally shows no or only small changes, in which so far no regularity could be detected.

Viscosity is perhaps the figure in which a change is first to be detected. Whilst the properties after vulcanisation often remain the same for a year or more, and only begin to change by longer keeping, the viscosity often begins to decrease sooner. Most first grade samples (crepe or sheet) remain constant in viscosity during several months or a year, but then gradually show a decrease, which seems to continue slowly on further keeping.

It is interesting to state that in some cases we observed an increase in viscosity, for which an explanation is still wanting. The following figures for a sample of smoked sheet with the ordinary nearly constant properties, for one crepe with a somewhat, and for two crepes with a very markedly increasing viscosity may serve as examples.

		I Smoked sheet	II Crepe	III Crepe	IV Crepe
After	1 week	33	17 $\frac{1}{2}$	28 $\frac{1}{2}$	25 $\frac{1}{2}$
"	2 weeks	—	20	33 $\frac{1}{2}$	30 $\frac{1}{2}$
"	3 "	—	—	41	34 $\frac{1}{2}$
"	4 "	33 $\frac{1}{2}$	21 $\frac{1}{2}$	—	—
"	5 "	35 $\frac{1}{2}$	22 $\frac{1}{2}$	42	38 $\frac{1}{2}$
"	6 "	—	22 $\frac{1}{2}$	44 $\frac{1}{2}$	43
"	7 "	35 $\frac{1}{2}$	24	44	32
"	8 "	—	22	48	48
"	9 "	37	26	48 $\frac{1}{2}$	49
"	16 "	—	25 $\frac{1}{2}$	53	62
"	20 "	—	—	57	59 $\frac{1}{2}$

The above statements all relate to estate-samples, prepared in the ordinary manner, and taken at random from the output of a large number of estates. While investigating different methods of preparation, one has, of course, also to study the keeping qualities of the product, and data have already been collected on several points. In general, these data do not point to a large influence of the method of preparation on the keeping qualities of first grade rubber, contrary to the fear that is often shown in this respect. Traces of special coagulants, such as sulphuric acid or alum, were not found to cause larger changes than the ordinary dose of acetic acid; neither did exaggerated crepeing, which is so often objected to by those at home, cause any marked or rapid deterioration in the raw product.

See for instance O. DE VRIES, Arch. 4 (1920), 210.

Whilst therefore the widespread fear of deterioration of the rubber by factors in the preparation seems exaggerated, there is no doubt that in special cases deterioration may occur to a very large degree. Several striking examples, caused by faults, or resulting in tackiness, will be treated in the next paragraphs; heavy deterioration by a specially noxious coagulant was treated in § 91, whilst examples of deterioration in the lower grades are given in § 179 and 183.

Packing the rubber only when quite dry and in dry chests, taking care that the chests do not get wet during transport or in a damp godown, and storing the rubber in a dry place with sufficient ventilation, especially between chests and floor, are the most necessary precautions for keeping rubber.

Recommendations for the storing of plantation-rubber see S. MORGAN, *Mal. T. & R. J.* 7 (1918), 1023; also *I. R. J.* 56 (1918), 831.

B. J. EATON (*Agric. Bull. F. M. S.* 7 (1919), 226 found the effect of storing raw rubber in the tropics small or possibly negligible, though the market value is affected, as pale crepe darkens considerably, whilst spots may develop on crepe and mouldiness on smoked sheet. Samples stored for two to three years, however, showed deterioration in quality, whilst the rate of vulcanisation appeared generally to become slower.

§ 164. Effect of light and sunlight.

Light, and especially daylight, is one of the factors that are regarded as harmful to the rubber; direct sunlight can spoil rubber completely. In former years, however, a much exaggerated fear reigned in this respect. The effect of ordinary subdued light in a factory or storehouse is so small that it may be neglected in practice. Of course, too strong light, or direct sunlight, should be avoided; but the special care to provide the drying sheds with red curtains or windows of red glass (instead of using ordinary white curtains) may be regarded as a fancy dating from the times that rubber was a very costly and high priced article.

Even the effect of too strong daylight in making the colour of the crepe somewhat less pale need cause no great fear; it is the course of things for all pale crepe in time to get somewhat darker, and the markets in Europe, where only crepe of some months old is known, are not so particular on this point as the Eastern markets, where the eye is spoilt by the very white colour of fresh crepe.

Whether strong daylight affects rubber more than very subdued light during the relatively short time that it is hung to dry has not yet been thoroughly investigated, nor do we know what is the effect of different quantities of light when storing rubber for a long time.

Direct sunlight on drying and already dry rubber should be carefully avoided. One must think not only of windows on the sunny side of the factory or storehouse, but also of fissures and holes in walls or roof, through which at a certain moment of the day a beam of sunlight may strike the rubber. Tackiness may be the result (see § 169), and tacky streaks could sometimes be traced to such a ray of light repeatedly striking the rubber. Such a ray of light may easily escape notice, as it perhaps only enters during a short time of the day.

See for instance B. J. EATON, Bull. F. M. S.* No. 17 (1912), 25.

Direct sun on rubber for some hours is sufficient to lower the viscosity greatly and sometimes even to reduce it to much below 10 units; if the exposure lasts long enough the rubber becomes weak and sticky and at last completely tacky. The inner properties are at the same time greatly affected; the rate of cure is much retarded, and the tensile strength falls off considerably with a longer exposure. A difference in the slope has not yet been recorded.

Apart from the stickiness, which very much damages the outer appearance of the rubber, the inner qualities are also much affected.

G. S. WHITBY (VIII Int. Congr. 25, 617; also I. R. J. 45 (1913), 1043 and Z. Koll. 12 (1913), 191) mentions a sample of rubber, exposed to the sun, which after 3 months became tacky and showed an increase in resin-content from 2.63 to 3.23 %; 9 months later the resin-content was 8.33 %, whilst the surface had become dry, shiny and smooth again.

It is the custom on many estates to brush the sheets with water when they come from the smoke house to remove ash and dust; some estates then put the sheets for a short time out of doors, in the sun, to get them dry quickly. No influence of this short sunning on the inner properties could be detected in comparative experiments; but still, as longer sunning is so harmful, the procedure does not seem advisable.

The effect of sunlight on latex has been treated in § 38. When thin films of latex are put in the sun, they coagulate or dry up; such rubber shows a normal tensile strength and does not seem to deteriorate.

B. J. EATON, J. GRANTHAM and F. W. F. DAY, Bull. F. M. S. No. 27 (1918), 79.

On the effect of sunlight on moist coagulum, as on latex, our knowledge is still very lacking.

§ 165. Influence of heat.

Heat too is one of the factors which in general is harmful to rubber. Concerning this, however, too great an anxiety is often shown; one forgets that the rubber, in the course of manufacture and especially in vulcanisation, has to undergo great heat, and that it does this brilliantly. Heating at lower temperatures, although the exterior to some extent suffers, need not therefore affect the inner properties, especially those after vulcanisation.

This is only true so long as the heat works in a purely physical way and does not cause anything more than a disaggregation, which possibly may lower the viscosity, but does not affect the properties after vulcanisation. If the conditions are such that oxydation, decomposition of the rubber or of the non-rubber constituents takes place through heating, then the consequences may be noticeable in vulcanisation.

We have discussed the results of heating latex in § 85 and 100; in § 120 we have spoken of the influence of heating during crepeing, that is on the moist coagulum; and in § 125 and 145 we treated the drying of crepe and sheet by heat.

We have here to treat the effect of heat on the dry, finished product. On dry rubber heat is only harmful when the temperature rises high; and the effect is stronger in proportion as the air has more access to the rubber and as more oxydation can take place. Short heating only produces a marked deterioration at 85° C or higher; for more prolonged drying the limit seems to be somewhat

lower, but in any case 50—55° C is a safe temperature-limit for drying houses, and when this limit is passed, a weak and sticky exterior all too soon gives a warning, long before the inner properties, especially the properties after vulcanisation, are noticeably affected. The viscosity seems to be somewhat lowered by heating above 60°, and only decreases markedly (at least after short heating) when the temperature reaches the neighbourhood of 80° C. The rate of cure and slope are unchanged; only when the rubber is very strongly attacked, a small decrease in the rate of cure is found. The tensile strength also decreases only at higher temperatures, probably in connection with oxydation or decomposition phenomena.

On the effect of different temperatures on dry rubber during short periods (1 to 5 hours) see O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 553 and 560.

Longer action of higher temperatures, with and without smoke, has not yet been systematically studied, though such „heat tests” on raw rubber might perhaps lead to valuable results, especially if not only the properties after vulcanisation, but also the viscosity, swelling properties and solubility, besides eventual chemical changes, were studied.

On the effect of a short heating to 100° C on the properties of the unvulcanised rubber see V. HENRI, Le Latex, page 329, also C. Gp. 1920, page 10198; further § 230.

§ 166. Faults and deterioration in crepe-rubber.

Faults in crepe-rubber may be many and of various kinds. Accidental admixtures caused by some oversight or negligence are of course of no general importance, though they may cause a lot of trouble to the adviser who has to find out of what they consist, and often needs all his detective imagination to track their cause.

When, for instance, some red-lead from the repairs to a water-pipe has got into a crepe, light red spots may be caused which are very similar in colour to some of the spots caused by moisture or slow drying; and as, generally, the repairs are already forgotten by the time the crepe is sorted and the spots discovered, a special genius is required to solve such and other cases.

Pieces of cloth, cotton waste for cleaning the machines, or parts of the clothes of the coolies will eventually get into the rubber and cause grey brown spots, which are easily identified microscopically, though it is often less easy to convince some managers that such things really occur in their well managed factory. Grease or oil from the bearings of the rolls may get into the rubber, and such rubber must be sorted out with care, as the properties are badly injured. Happily the newer types of crepeing-machines are generally so built that grease or oil does not come into contact with the rubber, so that such cases are now very scarce.

B. J. EATON (Agric. Bull. F. M. S. 7 (1919), 225) investigated the effect of oils or grease when adding them to the rubber shortly before mixing and vulcanisation. In one case an acceleration in rate of cure was found, due to alkalinity of the grease.

The effect of such substances, when incorporated in the rubber for a long period, may be quite different, especially when they contain traces of copper, see § 169.

Other admixtures of dirt of some kind may cause streaks and spots. We may mention, for instance, one case in which an estate had dark streaks in the crepe, the cause of which could not be discovered. On closer examination it struck us that the streaks were all found at a fixed distance from the edge of the crepe; and further examination led to the discovery of the cause, viz. a small leak in the water pipe above the rolls, from which from time to time drops of water with some dirt and rust dripped, especially when the water flow was opened after an interruption.

Such cases may be very interesting and stimulating for the adviser who has to clear them up; but we will not treat them further here, as they are of no general importance as regards the properties of the rubber. Only some of the most important faults and their influence on the properties of the rubber will be treated in the following paragraphs.

§ 167. Spots and streaks in crepe from faulty preparation.

Several kinds of spots on crepe may be caused during preparation.

When the latex has clotted or curdled during transport, and is not carefully strained, the lumps of pre-formed coagulum may be later seen as yellowish or violet brown spots in the crepe. Curdling shortly before or during the admixture of the acid, however, mostly does not lead to streaks or clots, probably because the small clots are still weak and evenly distributed through the coagulum. We will see in § 176 that partial coagulation gives a rubber of somewhat inferior properties; and as they range under this head, the spots caused by true pre-coagulation would make the product somewhat inferior. Their quantity, however, is generally small, and when they are mixed up with the rest during compounding, no decrease in properties after vulcanisation is generally found. When testing the spotted patches separately, a deviation as in pre-coagulated rubber may sometimes be detected, but generally the difference in properties between the normal and the spotted parts is negligible.

The violet surface-discolouration (see § 12 and 107) may cause dark violet or blueblack spots and streaks. This discolouration is caused by the oxydation of some non-rubber substances, and the rubber itself is not attacked. Whether these coloured substances have any influence on the vulcanising properties, is not yet certain; no deterioration could so far be detected (see § 12), but this might be ascribed to the fact that their amount is so very small. Though therefore the small amounts of oxydation-products cause a strong and very striking discolouration or streaking of the product, the harm to the rubber is nil or negligible, and the more so when the whole crepe is mixed and vulcanised. By the use of bisulphite these spots are avoided, and they therefore are found mostly in crepe from remnants of latex, skimmings, damaged sheets etc.

Especially during and after the war, when good rolls were difficult to obtain, some trouble was experienced with nearly black streaks caused by rolls of weak iron. The streaks are often only formed when the crepeing is interrupted or when the machine runs without rubber. As, however, before starting the milling the rolls are always cleaned with a

piece of scrap rubber, the dirt is mostly taken up by this piece and the clean first grade crepe remains free from it. Some rolls, however, were of such bad quality that the whole crepe took a somewhat greyish tint, and we have even seen rolls which after a few times rolling made a white piece of crepe completely dark black.

The crepe, on testing, is generally found to be of normal quality, and it is not to be expected that the very finely ground particles of iron or graphite would really injure the quality, though, of course, the rubber is not absolutely clean, and lacking in appearance.

The orange-yellow colour of crepe, caused by clayey water, was treated in § 39. The properties are generally not affected by this discolouration.

§ 168. Spotting of machined crepe.

After machining, during drying and also in the dry state crepe may also get spotted. In contrast to sheet, the ordinary surface moulds, such as *Penicillium* and the like, in practice never develop on crepe-rubber. Still it may be mentioned that crepe is not wholly unsusceptible to surface-mouldiness: when kept sufficiently moist (for instance freshly rolled crepe, kept in a closed vessel with some water), surface-moulds may develop, and this may even, though very seldom, occur on estates, when blocks of wet crepe are kept for some reason or other. The moulds, during drying, disappear, but their effect may be visible in a light bluish hue on the crepe. As it is only a question of a superficial growth, no real harm to the rubber need be feared.

Some of the most common spots on crepe are formed during drying, namely when drying is too slow during periods of wet weather, or when the crepe is not rolled thin enough. Orange, pink, violet, blue and dark purple spots may develop, most intensively in the thickest parts of the crepe. Similar spots may be formed if the dry, clean crepe becomes moist after its despatch, for instance from rain or seawater on the chests, or from storing on a cement floor in a moist godown, and also from packing in chests which are

not dry enough. These spots are caused by micro-organisms.

The micro-organisms causing these spots were studied by K. BANCROFT, Bull. F. M. S. No. 16 (1913); the investigations were repeated and extended by A. SHARPLES, Bull. F. M. S. No. 19 (1914). See also P. ARENS, Z. Bakt. II 35 (1912), 465 and Rubb Rec. 1914, page 397; N. L. SÖHNGEN and J. G. FOL, Z. Bakt. II 40 (1914), 87; F. C. VAN HEURN, Arch. 2 (1918), 119.

Microscopic examination of the spots is easiest made by swelling or dissolving the rubber in benzene or xylol; for more elaborate methods see SHARPLES, l. c.

These micro-organisms form strongly coloured matter from the non-rubber substances, and as long as the attack only lasts a short time, the exterior of the rubber may be largely damaged by the discoloured spots, but the properties after vulcanisation, and even the viscosity, are not harmed. The following examples of spotted crepes with unchanged vulcanising properties may be quoted.

	Tensile strength	Standard time of cure	Slope	Viscosity
I. Unspotted control. . . .	1 33	120	36	16 1/2
Piece with many red, yellow and green spots . .	1.30	120	37	14
II. Unspotted control. . . .	1.34	115	35	29
Piece with small violet spots . .	1.27	110	34	27 1/2
III. Only slightly spotted part of crepe	1.31	140	35 1/2	18 1/2
Part with many violet and yellow spots . .	1.30	> 140	34	23 1/2

As a specially interesting case we mention a sample of lump crepe of which large parts had taken a dark blue inky

colour. In comparing these pieces with the unchanged, greyish yellow parts of the same crepe, the difference in in properties was found astonishingly small:

	Tensile strength	Standard time of cure	Slope	Viscosity
Unchanged parts .	1.40	90	36	27
Dark blue parts .	1.39	95	36	24 1/2

Apparently a relatively small quantity of intensely coloured matter has been formed, which as an admixture to the rubber does not influence its properties.

In other cases a change sets in, and apparently the rate of cure is the first property to be affected. For instance:

	Tensile strength	Standard time of cure	Slope	Viscosity
I. Unchanged parts of crepe . .	1.29	> 130	35	28
Orange spotted parts . . .	1.35	< 140	35	27
II. Unchanged parts of crepe . .	1.27	125	37	19
Dark blue spotted parts . .	1.24	140	38	17

In certain cases the effect may even become serious, and the properties may be very badly injured. The following examples illustrate this clearly enough; the nature of the decomposition that causes such a deterioration, and the organisms producing it, as distinct from those that cause only an innocent (though very striking) discolouration, are not yet known.

	Tensile strength	Standard time of cure	Slope	Viscosity
I. Unchanged parts of crepe . .	1.22	90	—	22
Red and green, strongly discoloured part .	0.96	125	—	8½
II. Unchanged parts of scrap-crepe.	1.40	> 105	36	46
Discoloured parts of same. . .	1.26	135	37½	23
Strongly discoloured parts.	—	ca 160	38	—

B. J. EATON (Agric. Bull. F. M. S. 6 (1917), 152; J.S.Ch.I. 36 (1917), 1222; Bull. F. M. S. No. 27 (1918), 163) found that the development of spots on still wet, matured crepe greatly retards the rate of cure. He concluded that the micro-organisms destroy the accelerator formed in maturation, as he did not find a decrease in rate of cure when spots had developed on ordinary crepe.

From our above mentioned figures it is however clear that when the spots have time enough to develop, the rate of cure of ordinary crepe may also be retarded greatly. That wet thin crepe, when rolled up so that spots develop, in some cases keeps nearly the same rate of cure, might be caused by a balance between acceleration by maturing and retardation by development of spots. The conclusion of EATON, that the micro-organisms in matured rubber first use up the accelerators (causing retardation), but in ordinary crepe the proteins, which have no influence on the rate of cure of the rubber, was not proved by chemical analysis, and would need further corroboration.

That the rubber is seriously attacked in cases such as described in the last table, is also clear from the loss in weight, which may amount to 4 and 5 %.

See B. J. EATON, J. S. Ch. I. 36 (1917), 1223, and Bull. F. M. S. No. 27 (1918), 169. In one experiment we found a loss in weight in spotted crepe of more than 3 %.

The micro-organisms are aerobic (need air for their growth) and therefore only develop on the surface, where air can penetrate. The interior of blocks or thick slabs, when kept moist for a long time, is not attacked, and of tightly rolled sheets only the outer parts are liable to spotting. Crepe, owing to its irregular surface, generally includes enough air, when rolled up tightly, to allow the development of these micro-organisms also in the interior of the roll.

B. J. EATON, *Agric. Bull. F. M. S.* 5 (1917), 178; *ibid.* 6 (1917), 152; *Bull. F. M. S. No. 27* (1918), 164.

The spots may develop on fresh wet crepe, but also on dry crepe, even when packed. The micro-organisms seem to be present universally enough, and a sufficient degree of moisture is the only necessity to enable their growth. Whether the crepes were spotted before being packed, or got so in the chests during transport, can generally be decided by investigating where the spots are found: if only the outer layers in a chest are infected, and the spots diminish towards the interior, the fault may be accepted as having originated after packing.

On the artificial development of spots on dry rubber after moistening it, see B. J. EATON (*Agric. Bull. F. M. S.* 5 (1917), 177) who studied this effect at tropical temperatures.

Cases of spotting, caused by chests that got wet, are described and illustrated by F. C. VAN HEURN (*Arch.* 2 (1918), 119).

See further the extensive discussion of the causes of spotting by S. MORGAN, *Prep. Pl. Rubber*, page 152.

§ 169. Tackiness.

Stickiness and tackiness may develop from very different causes, of which the principal are:

- 1) stickiness caused by too high temperatures during drying;
- 2) stickiness caused by heating during milling;
- 3) tackiness caused by infection from soil or water;
- 4) tackiness caused by copper compounds;
- 5) tackiness caused by sunlight.

Several other causes are mentioned in literature, but do not seem to play any role in actual estate-practice.

1). *Drying at high temperatures.*

In the first place crepe may become superficially weak and sticky when too high temperatures are used during drying; the colour then becomes darker and more brown, and at last the crepe may get an odour like that of caramel. If the crepe is dried in a vacuum (see § 125), ordinarily one finds that a beginning of such alterations takes place; in the drying house, even when drying with hot air, this occurs only very exceptionally.

The inner properties of the crepe suffer relatively little, far less than the altered exterior would make one suppose. Superficially the crepe can become quite weak and brown without deterioration in the tensile strength, rate of cure or slope occurring, and even the viscosity is often not at all affected, frequently only to a small degree.

Although the exterior has become far less attractive and the crepe is difficult to handle because of its stickiness, a marked deterioration in inner properties need not have taken place. Indeed, besides the fact that many estates have dried their rubber in vacuo for many years, or have made it weak by heating before pressing it into blocks, without any claim as to its quality having been heard of, this conclusion is further corroborated by the treatment in rubber-factories, where the rubber is mostly dried completely, often in vacuo, before vulcanisation, by which procedure it also becomes weak and sticky. Rubber manufacturers, who know how much heat the rubber must and can stand in vulcanisation, are far less afraid of a little heating than planters are.

Figures for the effect of different temperatures on the rubber are given in § 125 and 145, whilst in those paragraphs it was also stated that too high temperatures or too long heating in the air can seriously damage the rubber.

2). *Stickiness by milling too hot.*

Another, closely related sort of stickiness arises because of insufficient cooling with water during milling. In good first quality crepe much has to happen before it becomes so warm that the exterior suffers; in estate-practice this seldom or never occurs. The inner properties only deteriorate by excessively long and warm mangling, so that the

crepe becomes decidedly weak; first the viscosity decreases, ultimately the tensile strength, the rate of cure and the slope may deteriorate.

See O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 547 and 558. Compare also § 120.

The fact that the lower grades are more sensitive in this respect will be treated in § 185.

3). *Tackiness from infection.*

In contradiction to the above cases of stickiness, which, at least in first quality crepe, are not so dangerous for the properties after vulcanisation, there are others in which actual deterioration does take place.

A dangerous sort of stickiness is caused by infection and produces the marked deterioration in the properties of earth-rubber and probably also of the poorer types of rubber from washings (see § 183 and 179).

The nature and course of this infection are not yet accurately known, but the figures in § 179 and 183 should be sufficient to show that the rubber can be greatly altered in quality by these agencies, indeed to such an extent that under unfavourable market conditions the production of these grades is not to be recommended.

Coagulum from good latex—earthrubber, by the way, is really nothing else—can greatly deteriorate from keeping under ground or by infection in other ways. An example may be given of already rolled sheets which had fallen during transport and lain on the ground under some shrubs for several months:

Tensile strength about	0.30 K.G.
Viscosity	2 to 4½ units

so that from thus lying on the ground in the rain, etc. a first grade rubber had deteriorated to an inferior product with a tensile strength and viscosity far below those of ordinary earthrubber. The rubber was quite sticky to feel, and gave a weak, black crepe.

On the contrary keeping under water seems not to affect the inner properties so quickly. For example a large lump of rubber torn from the coagulum by thieves and thrown

into a rice-field, in which it had lain an unknown time under water, gave the following figures on testing:

Tensile strength	1.36
Standard time of cure	70
Slope	33 $\frac{1}{2}$
Viscosity	68

therefore the properties of matured rubber of good quality.

Whether the deterioration in quality is only to be ascribed to the direct influence of organisms, and which organisms these are, has not yet been investigated. The harm can spread further after the rubber has been creped and dried, so that the samples steadily become more and more sticky; examples of this are given in § 183.

M. K. BAMBER (Circ. R. B. G. 3 (1906), 297) mentions bacteria, fungi and an oxydising enzyme in liquified rubber, and found that tackiness can be communicated by inoculation.

The growth of a number of micro-organisms on rubber was studied by N. L. SÖHNGEN and J. G. FOL (Z. Bakt. II, 40 (1914), 87) who showed that two species of *Actinomyces* can feed on the caoutchouc-hydrocarbon itself, decreasing the viscosity of the rubber somewhat.

4). *Copper compounds.*

A fourth kind of stickiness, which readily turns into a real tackiness, is caused by traces of copper compounds, which promote oxydation of rubber in contact with the air, and cause it ultimately to become entirely resinous.

Especially in former years, when the pernicious influence of minute traces of copper was not yet discovered, trouble from this source was often encountered, due to corroded copper rolls, or to oil which contained traces of copper. Many times one saw a local corrosion of the rubber starting from the point where the copper particles lay; if these were distributed by crepeing, the rubber would become tacky over the entire surface.

The following figures give an example of how strongly a slight trace of copper salt may affect the rubber. The crepe was prepared from latex to which a trace of copper sulphate was added, and examined a month after preparation, when externally it appeared wholly normal and free from tackiness.

	Tensile strength	Standard time of cure	Slope	Viscosity
Control	1.37	115	36	28 1/2
With 1/100 gm of copper sulphate per liter of latex	1.27	125	37	20 1/2
With 1/10 gm of copper sulphate per liter of latex	1.11	135	38	7

After 6 months the last sample was already very sticky, with a viscosity of scarcely 2 1/2 units; while in the second the tensile strength had somewhat deteriorated and the viscosity fallen to 12. The control had remained unaffected.

After two years keeping the first two samples were unchanged in exterior and not at all sticky; the properties of the sample with a trace of copper sulphate had, however, deteriorated markedly. The figures were:

	Tensile strength	Standard time of cure	Slope	Viscosity
Control	1.30	120	38	23
With 1/100 gm of copper sulphate.	1.04	< 135	40	6 1/2

The third sample had become completely sticky and could no more be vulcanised; the viscosity had decreased to 2 units, whilst 40 % had become soluble in acetone.

On tackiness caused by traces of copper see for instance B. J. EATON, Bull. F. M. S. 17 (1912), 28; S. MORGAN, Prep. Pl. Rubber, page 161; A. VAN ROSSEM, Comm. Delft IV, page 121.

On the effect of copper salts see further C. P. FOX, J. Ind. Eng. Ch. 9 (1917), 1092; also I. R. W. 57 (1917), 18 and I R. J. 54 (1917), 606.

Tackiness caused by traces of copper is accompanied by a fairly rapid oxydation; increases in weight of 7 to $13\frac{1}{2}\%$ were found in the course of 14 weeks.

S. MORGAN, Prep. Pl. Rubber, page 164.

It is interesting to note that treating the trees with Bordeaux mixture, if done with adequate care, does not introduce traces of copper into the latex to such an extent that tackiness of the rubber is the result.

A. SHARPLES, Agric. Bull. F.M.S. 3 (1915), 447; also I. R. J. 54 (1917), 193.

It may be remarked that other metals have no such influence on rubber. For instance traces of manganese, added either in the form of manganese salts to the latex or used as potassium permanganate to wash and disinfect sheets, are not known to cause any tackiness.

K. GORTER (Med. Rubber II, page 48; Rubb. Rec. 1914, 388) found the same, very small, amount of manganese in tacky and sound parts of one sheet.

Nickel salts also, when added to the latex prior to coagulation, did not cause tackiness in our experiments on this point.

Tackiness caused by iron salts (rust from the rolls or from iron collecting cups) was mentioned by B. J. EATON (Bull. F.M.S. No. 17 (1912), 23).

5). *Tackiness from sunlight.*

Finally tackiness may be due to sunlight. We have treated this point already in § 165, and described the changes in the inner properties. Such rubber had also deteriorated without hope of recovery.

Other causes.

In the course of years several other causes have been put forward as causing tackiness. In former chapters we have already mentioned cases of tackiness caused by soaking the coagulum or freshly machined rubber in alkali (§ 106, page 236), by coagulation with rather strong doses

of hydrochloric acid (§ 89) and an acid volcanic water (§ 91). On the contrary, sulphuric acid and alum did not give us tacky rubber (see § 86 and 88).

D. SPENCE (Z. Koll. 4 (1909), 71) mentioned sulphuric acid as causing tackiness, when keeping Funtumia-latex with a small amount of sulphuric acid for one month at 35°. Such an influence was, however, not observed by F. FRANK and E. MARCKWALD (Z. Koll. 5 (1909), 189), when coagulating Funtumia-latex with sulphuric acid.

Defective coagulation has been supposed to cause tackiness by many authors. For Hevea-rubber, however, no cases are known in which any divergent type of coagulation (apart from harmful coagulants, see above) produced tackiness.

See PH. SCHIDROWITZ, Rubber, page 136; G. BERTRAND, C. Gp. 1908, page 1941. On the supposed influence of a lowly polymerised part of the caoutchouc, as causing tackiness, see F. FRANK and E. MARCKWALD (Z. Koll. 5 (1909), 190).

Enzymes, proteins and sugars have all been named as causing tackiness, but more in the form of hypotheses, for which no proof has yet been brought forward.

Oxydising enzymes were regarded as the cause of tackiness by M. K. BAMBER (Lectures 1908, page 201), who however produced no definite proof. D. SPENCE (ibid.; further Z. Koll. 4 (1909), 71) rejected this supposition.

PH. SCHIDROWITZ (Rubber, page 119) names sugars as substances causing inclination to tackiness if they are not sufficiently removed.

Some of these causes may perhaps cause tackiness in rubbers other than Hevea; in fact, too much has been generalised under the name of tackiness, and changes all ending in some kind of stickiness or tackiness, but different in nature, have been confused.

Anti-tacky expedients.

There have repeatedly been claims made for treatments which would restore tacky rubber.

It is evident that this is impossible, at least for the above cases 3 to 5. Rubber which has become oxydised or decomposed cannot (at least in estate-practice) be restored. Of course,

by treating it with different substances, the tackiness can be made less visible or, by recrepeing, the portions can be equally distributed over the whole surface, and apparently a bettering of the condition be effected; but the inner properties are and remain harmed, and the tackiness in the course of time is again clearly discernible, and afterwards becomes worse, since the infection is spread equally over the whole sample.

Efforts in this direction deserve no support, and for the good name of plantation-rubber it cannot be too strongly recommended, that all rubber which is tacky should be either destroyed or offered on the market as „tacky”; in the mean time proper measures can be taken to avoid further tackiness.

On a supposed process of restoring tacky rubber to its normal state see for instance I. R. J. 48 (1914), 174.

Chemical changes.

About the chemical changes, accompanying tackiness, relatively little data are available, and the different types of stickiness have not been separately studied and distinguished.

That oxygen is necessary for the development of tackiness, at least for certain types of tackiness which are directly oxydation phenomena, may be regarded as sufficiently proved; the amount of oxygen taken up by the rubber may be small (less than 0.5 %) but with increasing tackiness may reach figures of 2—3 %, and finally much higher.

See S. J. PEACHEY, I. R. J. 45 (1913), 361; E. FICKENDEY, Z. Koll. 9 (1911), 81; HEIM and MARQUIS, Ann. Pl. Ind. Ch. (1915), 108; K. GORTER, Med. Rubber I (1911) and II (1912), and Rubb. Rec. 1914, 385; M. KERBOSCH, Teysm. 26 (1915), 42 and Med. Rubber III (1914).

A. VAN ROSSEM (Rubb. Ind. 1914, page 149; I. R. J. 48 (1914), 172; C. Gp. 1913, page 696; also Z. Koll. 12 (1913), 78; see further Comm. Delft, Part IV) made a special study of these phenomena, and holds the opinion that a certain degree of depolymerisation of the caoutchouc has to precede the oxydation, which depolymerisation is accelerated by the presence of oxygen.

When tackiness reaches a sufficient degree, the acetone-extract may greatly increase. In completely sticky rubber 90% and more may have become soluble in acetone.

H. BROWN (Rubber, page 78) mentions a case in which the sound parts of a crepe showed an acetone-extract of 2.9% and the tacky parts 8.2%, containing a considerable quantity of free acids of resinous nature.

He further mentions analyses by M.K. BAMBER in which a „very tacky” sample showed 1% more acetone-extract and protein than sound or slightly tacky samples.

G. S. WHITBY (VIII Int. Congr. (1912), 25, 615; also I. R. J. 45 (1913), 1043 and Z. Koll. 12 (1913), 190) mentions samples of tree-scrap, which became tacky and after six weeks showed a resin-content of 10—27%, which finally rose to even 78%, the samples again losing their tackiness and becoming shiny, smooth and dry, ultimately brittle. A tacky sample of ordinary crepe contained 6.59% resin and later 19.08%, when it had become less sticky; the viscosity was extraordinarily low.

In a sample of rubber prepared with some copper sulphate (added to the latex) we found after 1½ years keeping 93% to be soluble in acetone.

The rather complex physical changes accompanying tackiness, which may throw light on its nature and are of great importance in the study of the structure of rubber, will not be treated here.

On the study of tackiness see for instance D. SPENCE, Z. Koll. 4 (1909), 70; Lectures 1908, page 200; G. BERTRAND, C. Gp. 1908, page 1941; *ibid.* 1909, page 3216; F. FRANK and E. MARCKWALD, Z. Koll. 5 (1909), 189; A. VAN ROSSEM, Rubb. Ind. 1914, page 149; V. HENRI, C. Gp. 1910, page 4371; F. KIRCHHOF, Z. Koll. 13 (1913), 51; K. GORTER, Med. Rubber II and III, Rubb. Rec. 1914, 385; and the discussion in SCHIDROWITZ, Rubber, page 134.

§ 170. Faults in sheet-rubber.

Trouble from faults in sheet-rubber is certainly not less than with crepe. One great advantage of smoked sheet is that the brown smoke-colour covers and makes invisible many differences in shade, which may give so varying an exterior to unsmoked sheet (see § 149). Even the violet discolouration, caused by oxydation on the surface of the coagulum, becomes practically invisible when the sheets

are thoroughly smoked. The white or very light yellow tint of crepe is much more sensitive in this respect, and discoloured spots of different nature are much more visible on it.

Against this advantage in smoked sheet — smoking is often mockingly called the „cloak of charity” — this form of rubber has two distinct disadvantages, which tip the balance in the favour of crepe-rubber, as far as trouble with the exterior goes.

The first is that the form of sheet-rubber is of importance, and that every deformation remains visible, whilst with crepe this can be restored by recrepeing. Irregularities in the surface, gas-bubbles in the coagulum, folds, tears, loose pieces of rubber, are faults that can be completely repaired in crepe-rubber, but in smoked sheet they enjoy a—wholly unfounded—degree of attention from brokers and buyers, and form a welcome subject for claims and reductions of the market-price.

The second disadvantage of sheet-rubber is formed by the larger content of serum-substances, which cause such faults as greasiness, mouldiness, rustiness. These faults can doubtless be prevented by adequate methods of preparation, but nevertheless have caused, and occasionally still cause, a large amount of trouble and not unimportant financial losses.

The principal of these faults will be treated in the next paragraphs.

Tackiness may, of course, occur in sheet-rubber as well as in crepe; in fact, some of the examples mentioned in the foregoing paragraph related to sheet.

Spots, as we stated above, play a less important role in sheet than in crepe. Still, coloured patches caused, for instance, by *Bacterium prodigiosum* may occur on sheets, and spots caused by fungi may also be found. When the time between coagulation and drying is too long — for instance in sheets kept two nights before they are put into the smoke house (see § 139)—circular spots may be formed by a micro-organism growing in the coagulum about 1 mM. below the surface.

§ 171. Mouldiness.

Perhaps the most serious defect in sheet-rubber is now-a-days the great susceptibility to mouldiness of the output of many estates. In former years this defect did not so much trouble the planters, as the rubber was sent away from the estate before any mouldiness could develop; at the ports also there was little opportunity for getting mouldy, as the rubber was regularly and rapidly handled and shipped. It was only in rare cases that the complaints of „green” rubber were so loud and strong that they reached the producers in the tropics from oversea. During the war, however, when shipment was held up, this trouble made itself felt in the producing countries, and has perhaps formed one of the most important complaints. Now it is certainly true that sheet only becomes mouldy if it is left sufficiently long in a moist atmosphere; but where the transportation offers so much opportunity for getting moist (by rain, seawater, etc.) and where damp godowns or warehouses (although one does not approve of them) must be reckoned with, the duty of the estates evidently is to decrease as much as possible the susceptibility to mouldiness.

It may be assumed that the majority of cases of mouldiness are caused by chests getting wet during transport. If not only the wood of the chests gets wet but the water actually reaches the rubber, it is absorbed by the sheets, which then show large white or opaque patches, like partly dried sheets; and with mould developing on many places, a most unsightly lot of rubber is formed which may well terrify the buyer, though the real harm done is generally not very great.

That the chests should be thoroughly dried and preferably placed some hours in the sun before packing the rubber, is generally known.

It does not seem possible to make sheet-rubber wholly immune to fungi (as indeed is the case also for crepe): by keeping them in an atmosphere of sufficient moisture-content every one of the samples which we experimented with became mouldy. But there is a very wide range in this liability to mouldiness, since in an atmosphere of not too

high a moisture-content some rubbers become very mouldy and others not. This is very evident during the wet monsoon in our sample-collection, where sheets from a large number of estates lie side by side in drawers and cupboards. Some remain untouched by fungi, whilst others become somewhat affected, and still others are covered with a thick veil of grey or whitish moulds.

The susceptibility to mouldiness may be tested more methodically by placing pieces of the sheet in atmospheres of a suitable, constant moisture-content, after infecting them with the ordinary fungi; a comparison of different samples is easily effected in this way.

O. DE VRIES (Arch. 3 (1919), 346 and 371) used dessiccators with 7 and 14 % solutions of common salt. The first gives a rather wet atmosphere, in which only some sheets do not get mouldy; the second gives a rather dry atmosphere, in which only the most susceptible samples show an abundant growth of moulds.

The use of vessels with water to obtain a moist atmosphere is not to be recommended, as small local differences in temperature, caused by light, radiation etc., cause the formation of drops, independent of the hygroscopicity of the rubber, which obscure the result.

The fungus most generally met with on rubber in the tropics is *Penicillium glaucum*. A kind of *Aspergillus* may develop later on, and then grows also on sheets which the *Penicillium* left untouched.

It is worth while to mention that a heavy growth of moulds often disappears within a few days, if attacked by small animals of different species which greedily devour this rich repast. As the sheets are somewhat less susceptible to mouldiness after such an attack, this may cause some confusion, if not duly noticed.

Prevention of mouldiness.

From the above it will be clear that in sheet-preparation measures should be taken to make the product as little susceptible to mouldiness as possible.

One means of decreasing this susceptibility is a thorough soaking of the sheets in water, directly after milling. Soaking the coagulum or the partly rolled out sheets in water does not help so much (see § 136), as serum-substances are

again pressed from the interior to the surface during the final rolling, and form a new substratum for the moulds.

That indeed this procedure may greatly help to make the sheets less liable to mouldiness, can be easily shown in comparative tests, and is especially striking with unsmoked sheets. For instance after keeping for a week in a moist atmosphere (see above):

Control, not soaked in water	very heavily mouldy
Soaked in water for 3 hours	rich growth of moulds
” ” ” ” 24 ”	a little mouldiness
” ” ” ” 48 ”	practically no mouldiness
” ” ” one week	wholly free from moulds

See O. DE VRIES, Arch. 3 (1919), 346 and 371.

The second means by which the susceptibility may be lowered is smoking. Smoked sheets as a rule are less susceptible than unsmoked sheets, although, as every one who has to do with the rubber-market knows, among smoked sheets there are many that are susceptible to mouldiness. The trouble is that as yet it is not known what method of smoking and what smoke-constituents are most effective. Perhaps the wood or other material used may be the cause, or the method of firing and producing the smoke, or the temperature of the smoke house and other factors. Research in this direction is most desirable; as yet no explanation can be given why sheets from one estate become mouldy so much more easily than those of others.

It has been further tried to prevent mouldiness by treating the finished sheets with some disinfectant, such as creosote, formalin, permanganate of potash. These, however, give no satisfaction, and generally help only for a short time.

See S. MORGAN, Prep. Pl. Rubber, page 167; P. ARENS, Mededeelingen van het Proefstation Malang No. 5 (1913).

T. PETCH (Trop. Agric. 40 Suppl. (Jan. 1913), page 61) comes to the conclusion that potassium permanganate should not be used; when used in any strength in which it is a disinfectant it turns rubber tacky by oxydation, while in the strength usually recommended it has no effect whatever.

Influence on the properties of the rubber.

It may be expected that a superficial growth of moulds, perhaps only some weeks old, does not harm the rubber, as its attack is in the first place aimed at the layer of serum-substances on the surface of the sheets. In fact, an examination of ordinary mouldy samples in most cases did not show any deterioration in properties after vulcanisation, or even in viscosity. Even in a lot of rubber, received back from America, which had become very unsightly by moisture and moulds, the latter had caused no deterioration in properties. The figures were:

	Tensile strength	Standard time of cure	Slope	Viscosity
Unchanged parts	1.35	> 80	39	26
Wet parts, no mouldiness.	1.40	< 70	36	36
Mouldy parts	1.32	< 80	39	27
Dry parts with fresh moulds	1.43	75	38	31

The parts that remained wet for a long time had evidently matured to a certain degree and accordingly show a greater rate of cure and viscosity and a smaller slope. A distinct deterioration caused by the moulds is not apparent.

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 44 (1912), 1149 and 1198) also mention that an ordinary growth of moulds does not seem to harm the properties after vulcanisation.

Even whether a prolonged attack of moulds may injure the rubber is not yet sure. By keeping a growth of moulds on samples of sheet-rubber during a period of 9 months we observed the following changes in properties.

	Tensile strength	Standard time of cure	Slope	Viscosity	Moisture	Loss in weight of dry rubber
Smoked sheet, original	1.30	< 95	35 ¹ / ₂	24	0.82	—
After 9 months, kept free from mould.	1.27	90	37	20	0.50	1.0
Kept 9 months under heavy growth of moulds.	1.28	< 95	37 ¹ / ₂	18	2.2	8.6

The difference in tensile strength, time of cure and slope is negligible; in viscosity a small decrease is found. In view of the fact that the moulds had caused a loss of 8.6 % of the dry rubber this result is remarkable; ordinary rubber contains some 93 % of caoutchouc-hydrocarbon, part of which must therefore have been consumed by the moulds. This is still more apparent from the fact that the chemical composition before and after the attack of moulds showed only relatively small differences. We found:

	Moisture	Ash	Watery extract	Acetone- extract
Smoked sheet, original . .	0.70	0.32	0.50	2.6
After 9 months, kept free from moulds.	0.85	0.30	0.61	2.3
Same, after washing and crepeing	0.66	0.24	0.29	2.8
After 9 months under heavy growth of moulds . . .	0.76	0.22	0.62	2.9
Same, after washing and crepeing	0.68	0.14	0.32	2.6

We may add that in another sample we produced a loss in weight of no less than 15.5 % of the dry rubber by 1½ years' growth of moulds. The properties of such heavily attacked rubber have still to be determined.

Though it cannot, of course, be said that surface moulds are wholly without influence, the above data make it clear that the fear for mouldiness is at least much exaggerated, and this lends support to the conclusion that the influence of a short and superficial growth of moulds will be negligible.

§ 172. Greasiness.

By greasiness is meant a somewhat sticky and moist feel of the sheet; in a moist atmosphere such sheets may absorb so much moisture that little drops are formed on the surface, as if the sheets had sweated. The delimitation of the defect is, however, not very strict, as the transition from

sticky to dry surfaces is very gradual, and as a kind of stickiness or greasiness caused by heavy smoking is sometimes also brought under this head.

It would be best to confine the term greasiness to a hygroscopicity of the sheets caused by serum-substances which attract moisture from the atmosphere. This kind of greasiness is generally coupled with a strong tendency to mouldiness, and is prevented by soaking the sheets in water after milling so that the easily soluble, hygroscopic serum-substances are extracted.

These two defects—greasiness and mouldiness—however do not always go hand in hand. For instance one can have sheets on which drops are formed in a moist atmosphere, but which are only slightly susceptible to mouldiness. Whether this is due to sterilizing qualities of the smoke-constituents, or to other factors such as the composition of the non-rubber substances, is as yet unknown.

The details of the origin and the cause of greasiness are not yet known. So it remains to be investigated what serum-substances are the cause of this phenomenon, and what changes are caused, for instance, by the decomposition which takes place when the coagulum is rolled on the following day or allowed to mature. It is also still unknown what the influence is of smoking, for instance of smoke of different composition, or of very moist smoke from unsufficiently dried wood or from fires fed with grass or leaves so as to produce a thick smoke: such smoking also produces sheets which are moist on the surface, but this is not the greasiness meant in this paragraph.

Greasiness caused by hygroscopic serum-substances may gradually disappear on keeping the sheets for a long time, as if a slow decomposition of these serum-substances takes place. In the same way, greasiness is most pronounced on sheets that are rolled shortly after coagulation and is found only to a lesser degree or not at all when the time between rolling and coagulation is longer, or when the sheets are kept for some time in moist condition or in a moist atmosphere. The decomposition which gives a beginning of maturation in such cases seems to be accompanied by processes which destroy the hygroscopicity. It is very

striking that rusty sheets (see the next paragraph) always have a completely dry feel. Greasy sheets generally show the bright, clear colour that goes along with rolling shortly after coagulation and drying rapidly, whilst dry-feeling (eventually rusty) sheets have the dark colour accompanying slow drying and retarded preparation; the difference is especially marked in unsmoked sheet, but may be noticeable in smoked sheet also (compare § 149).

For estate-practice the most important point is that greasiness may be prevented by the same means as that applied for reducing the susceptibility to mouldiness, namely soaking the freshly rolled sheets in water.

Even dry sheets that show greasiness may be cured to a large extent by soaking them in water and hanging them to dry.

As far as is known, greasiness has no marked influence on the inner properties, at least not more than one might expect in connection with the methods of preparation which lead to it, and with the composition of such rubber (presence of hygroscopic serum-constituents). A direct deterioration of the rubber or a real harm to the inner properties is therefore not to be feared. As this defect is so often coupled with a large tendency to mouldiness (namely, in so far as the sheets are not sufficiently disinfected by the smoking), it is quite reasonable, and cannot be objected to, that greasy sheets are not classed under first quality and are not accepted without protest.

Greasiness is, however, so easily prevented that one may hope and expect that it will seldom or never more be seen.

§ 173. Rustiness.

„Rust” is the term applied to a thin invisible film on the sheets, which breaks and becomes visible when the sheet is stretched. On unsmoked sheets it has a yellowish white colour, on smoked sheets it becomes brown or rust coloured.

This film is formed by the growth of micro-organisms in the wet layer on the outside of the freshly rolled sheets.

These organisms decompose some of the serum-constituents, probably the sugars, and form a very voluminous jelly-like substance, which dries up to an invisible cohesive film.

That rustiness is caused by the growth of micro-organisms, was proved conclusively by H. J. HELLENDORRN (Arch. 3 (1919), 431) by artificially producing it under favourable circumstances (keeping the sheets in a moist atmosphere for 24 or 48 hours after rolling), by preventing it under otherwise favourable circumstances by disinfection, and by producing it on dry or disinfected sheets by direct infection. The micro-organism, causing rustiness, has however not yet been isolated and identified; the chemical changes accompanying its growth could not be further investigated yet.

The organisms which cause rustiness seem to be everywhere present, as rustiness occurs on all estates without showing the character of a plague, and could be produced artificially (by keeping the rolled sheets in a moist atmosphere) anywhere when an experiment was made. The organisms are aerobic, that is to say they grow only when sufficient air is present. They prefer dilute solutions of serum; sheets from diluted latex are accordingly more susceptible to rustiness than sheets from concentrated latex. Soaking the sheets in water after milling does not hinder the rubber from becoming rusty; on the contrary, such sheets may show rustiness to a very large degree, if the organisms have time enough to develop.

See P. ARENS, Arch. 1 (1917), 200 and 203; H. J. HELLENDORRN, Arch. 3 (1919), 426 and 434.

The organisms causing rustiness of course need¹ some time to grow and to form the layer of jelly-like substance, and naturally thrive only when the surface of the sheet is moist enough. Therefore the most efficient, and for estate-practice the most advisable means for preventing this trouble is to take care that the sheets are surface-dry a few hours after hanging them. *

On some estates it is customary, after rolling, to allow the sheets to drip somewhere in a dark corner of the factory and to hang them very close together. This is entirely wrong; the sheets should be hung in as windy a place as possible, if necessary outside, in the shade,

and then wide apart, so that they will surface-dry as quickly as possible. If it is not possible to get the sheets dry on the surface in a few hours, they must after this time be taken into the smoke house, where the drying by heat and smoke will delay the growth of the organisms, provided the ventilation of the smoke house during the first few hours is sufficient.

See P. ARENS, Arch. 1 (1917), 200 and 203.

That the rust-forming organisms are aerobic, was proved by direct experiments, and is also clear from several observations in practice. For instance, when keeping the coagulum overnight before rolling, the upper surface may become infected, and when the sheets, after rolling, are kept in a moist atmosphere, the surface that was exposed to the air during and after coagulation develops rustiness much more rapidly and strongly than the other side. In the same way a rusty sheet may show a rust-free bar in the middle, where the sheet hung smoothly round a stick, so that not sufficient air could penetrate. But on the other hand sheets may show a rusty bar, when they have hung loosely round the stick in the smoke house, so that moisture and air were present, and the smoke did not penetrate enough to prevent rustiness in that stage.

See H. J. HELLENDORF, I. c. Tightly rolled fresh sheets only develop rustiness on the outer surface and on places exposed to the air; sheets kept moist in atmospheres free from oxygen did not develop rustiness.

The most favourable temperature for the development of these organisms seems to lie in the neighbourhood of 40° C. This is of some importance in estate-practice, as it means that rustiness may develop to a larger degree when the sheets are placed in a moderately heated smoke house with insufficient ventilation, at least when the smoke does not hinder the growth of the organisms.

The effect of smoke on the rust-forming organisms is not yet sufficiently studied; a certain disinfection could be observed, but it is not yet certain whether smoke under all circumstances is a sufficiently effective disinfectant.

It is worth while to state clearly that rustiness is caused by a *decomposition* of serum-substances by micro-organisms, whilst greasiness arises when *undecomposed*, hygroscopic serum-substances dry up on the sheet. Soaking the fresh sheets in water may help to prevent greasiness but does not help against rustiness (on the contrary it may further the development of the micro-organisms).

In former years one was recommended to dip the freshly rolled sheets for a short time in hot water to prevent rustiness. This method, as a disinfection, may be perfectly understood from the above, but as the treatment is not favourable to the properties of the rubber (see § 140) it is much better replaced by rapid surface-drying in the air, and is now completely out of use.

Disinfection of the surface by chemicals such as formalin, chinolol etc. might be effective, but is more expensive than air-drying and therefore never resorted to on estates.

Adding disinfectants to the latex may help to prevent rustiness; the ordinary dose of bisulphite however is of no effect (see P. ARENS, Arch. 1 (1917), 201 and 203; H. J. HELLENDORF, Arch. 3 (1919), 432).

Influence on the properties of the rubber.

Rustiness itself produces no changes in the inner properties of the rubber. The thin layer of harmless substances is only found on the outer surface, since air is necessary to the growth of the organisms. The interior of the sheets is not affected, and after the sheets are once dry, the changes cease, while rusty sheets, probably in connection with the changes by which rustiness is caused, are not hygroscopic (see § 172).

As rustiness only occurs when the sheets are left in moist condition for some time after milling (say 24 hours or more) a beginning of maturation of course takes place, so that rustiness is usually accompanied by a somewhat greater rate of cure and often by a higher viscosity.

See O. DE VRIES and H. J. HELLENDORF (Arch. 2 (1918), 527 and 536), who investigated not only rusty sheets from estates, but also sheets artificially made rusty in different ways and under different conditions, and found no other changes in properties than these caused by the method of preparation.

On keeping rusty sheets for several years, no deterioration takes place and the properties change in the same way as in the non-rusty controls.

Rustiness therefore must be classed amongst the harmless defects, and should not form the base of any claim; the decomposition of serum-substances, by which it is caused, need not cause any more fear than maturation-processes and similar changes. Nevertheless, manufacturers and brokers are not yet convinced of the innocent character of the fault; and since rustiness is so easily avoided by following the above described methods — the only important point being to take care that the sheets are surface-dry within a few hours after milling — it is a much better policy for estates to take care that rustiness does not occur, than to run the risk that a buyer, although in reality unjustifiably, sees therein a motive for a claim or reduction in price.

§ 174. Gas-bubbles.

Small, eventually microscopic, bubbles that are sometimes found in sheet are mostly called air-bubbles. It is however more to the point to call them gas-bubbles, since bubbles really caused by air may be regarded rather as an exception, at least in later years.

Bubbles formed by air may be expected in the following cases.

1). Too rapid coagulation, by which the latex quickly becomes very viscous, and shortly afterwards solidifies. Air-bubbles, which were mixed mechanically with the latex during the filling of the pans or during the stirring in of the acid, have no time to escape and are enclosed in the coagulum. Probably this case practically never occurs at present; in former years, when undiluted latex was used in sheet-preparation, and the dose of acetic acid taken rather large, whilst strong solutions of acid (10 % and more) were the rule, a great deal of trouble was experienced from this source.

This defect forms a typical example of the relation between external appearance and inner properties. It is self-evident that a few air-bubbles, mechanically mixed with the latex,

cannot in the least affect the inner properties of the rubber. Still the distrust of buyers, even if it is not caused by a total lack of knowledge of the real nature of the defect, is in a sense understandable: this trouble can be avoided by proper methods of preparation, and if this mistake is made on an estate, why not others also, which are not so easily detected from the exterior?

2). Air-bubbles may further be formed by air escaping when the uncoagulated mixture of latex and acetic acid stands in a warm place. If a liquid is warmed, the solubility of gases is decreased, and so, when latex is cool and is set to coagulate in a warm place, bubbles of escaping air may be formed. Probably this case also belongs now-a-days to the great exceptions. It has, by the way, never been proved that the bubbles so formed are really filled with air and not with gases formed by the decomposition of serum-substances.

M. BARROWCLIFF (*Agric. Bull. F. M. S.* 1 (1912), 166) mentions bubbles caused by carbonic acid gas, developed from bicarbonates of magnesium or calcium in the latex, and forming bubbles either during rapid coagulation, or when the coagulating latex or the coagulum becomes warmer.

S. MORGAN (*Prep. Pl. Rubber*, page 173) enumerates a number of cases in which bubbles may arise, similar to the above.

In most instances the bubbles in sheet are filled with gases which are formed in the latex and the coagulum (for instance by micro-organisms); therefore in the first place carbonic acid, further probably nitrogen and some methane. On the composition of these gases very little is known as yet.

The gas-bubbles, formed by decomposition of serum-substances, are the most common form; the bubbles are sometimes as large as a pinhead, sometimes only to be identified under the microscope. When the sheets are held against the light they usually appear as small dark or black points; in reflected light they appear as white spots, as if the rubber were not entirely dry. The direct causes and the methods of prevention can—as might be expected from a trouble due to infection—vary greatly and may cause the

adviser much worry, since the factors which so promoted the growth of micro-organisms that a noticeable development of gas-bubbles was the result, are not always easy to ascertain later on. One may suspect insufficient straining, or a beginning of clotting, by which impurities are enclosed in the clots; or a beginning of the decompositions accompanying local bacterial action when too little acetic acid is used, or when the acid is stirred in unevenly.

See S. MORGAN, Prep. Pl. Rubber, page 170.

In most cases the trouble is avoided by following the method of preparation described in § 135 and 152: rolling the sheets shortly after coagulation, so that no time is given for the micro-organisms to develop and produce gases. The larger quantity of acetic acid used in rapid coagulation also helps, as it acts to some extent as a disinfectant.

The bubbles themselves, as inclusions of innocent gases, probably have no effect at all on the inner properties of the rubber; the processes by which they are produced (decomposition of serum-constituents, maturing etc.) generally cause a somewhat quicker cure and higher viscosity (see § 107 and 108) so that one may expect these also in sheets with gas-bubbles. Strictly comparable data concerning these points are however not available.

A third type of bubbles are the great blisters which may have the size of a pea or even larger. These arise from too high a temperature in the smoke house (see § 145), i.e. when the temperature in the first few days after coagulation runs above 70° C (158° F).

Exactly how the formation of these blisters is to be explained, is not yet known. It cannot be the purely physical phenomenon of expansion of smaller bubbles through heating, for the rise in temperature (only a few tens of degrees) cannot increase the volume so many times. Formation of water-vapour also cannot cause the bubbles, for the temperature is still too low. The most probable cause is the simple separation of gas from the serum of the moist coagulum, escaping because of the heating. The action of micro-organisms, which become active

at higher temperature and develop gases by decomposition-processes might also be suspected as a cause; but since disinfectants, such as a strong dose of formalin added to the latex, do not hinder the formation of these bubbles, which develop just as numerously and as large when so treated coagulum is dried at 75 or 80° C during the first days, it is not probable that micro-organisms play a role. The analysis of the gas from the bubbles does not offer an explanation. We have several times collected the gas from artificially produced bubbles (by hanging sheets to dry at temperatures above 70°), and found it to be air. This, however, does not prove that the originally developed gas was air also, for it may have diffused and been replaced by air.

Sheets with these bubbles have the properties of sheets dried at higher temperatures without such blisters developing (see § 145); any special influence from the gas-bubbles could not be detected.

CHAPTER XIII.

LOWER GRADES.

§ 175. General review of properties.

Amongst „lower grades” are comprised rubber types of the most divergent properties. Rubber from scum may often be considered on a par with first quality rubber, and amongst the lump and scrap varieties many good and often excellent lots are found, which are inferior to first quality only in colour. Bark- and earth-rubber, on the contrary, are nearly always contaminated by particles of dirt and often have a tendency to tackiness, while amongst the rubber from washings very poor types are found along with very good ones.

Figures 8 and 9 contain the values obtained in testing a large number of samples from different estates during the years 1916—1919, and give a fairly accurate idea as to what values may be found for the different types by our methods of testing. The figures for different types will be discussed in detail in the following paragraphs.

The range in tensile strength is great, from excellent values such as 1.45, which would be more than satisfactory in first grades also, to such low figures as 1.00 and even 0.80. In part this is due to an actual degeneration and deterioration of the rubber, but in other cases only the mechanical contamination with earth and pieces of bark is the cause. A poor tensile strength for these sorts, therefore, does not necessarily indicate an inferior rubber; a determination of the viscosity may help in such cases to decide what is the real cause (see § 237). Very dirty samples, which cannot be sufficiently cleaned by washing and recrepeing, may show extremely low values, but in such samples a determination of tensile strength, as, in fact, the whole testing by vulcanisation, is valueless and may just as well be left undone.

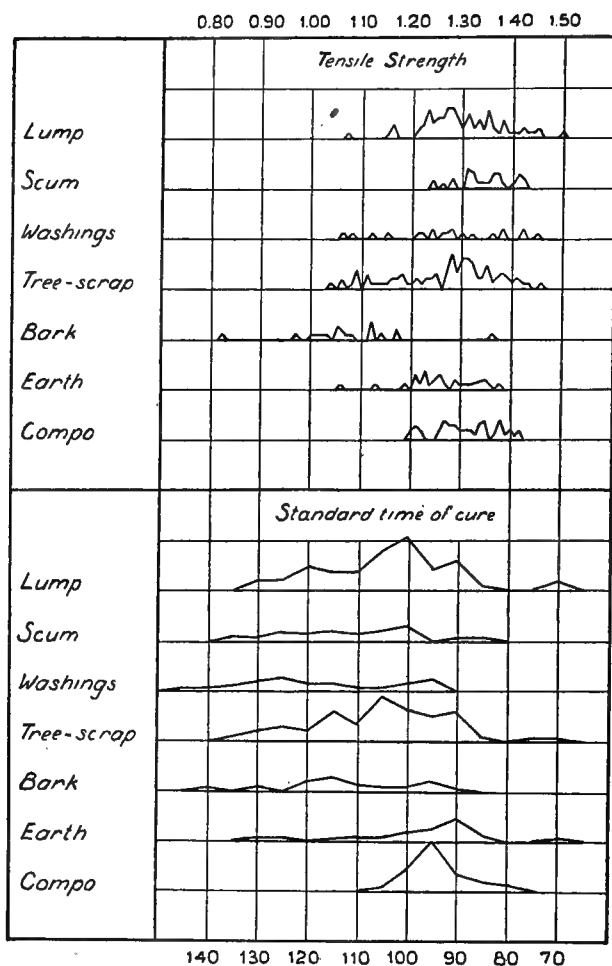


Fig. 8.
Tensile strength and standard time of cure for a large number of samples of different grades.

The values for standard time of cure lie mostly between 90 and 130 minutes, that is to say the normal figures for ordinary first quality crepe or smoked sheet. Really abnormal values are seldom met with; some slow curing rubbers may be found amongst the crepes from washings, whilst some rapid curing types are obtained when lump or tree-scrap are kept some time in moist condition before crepeing, so that maturation may set in. Pre-coagulation may give a

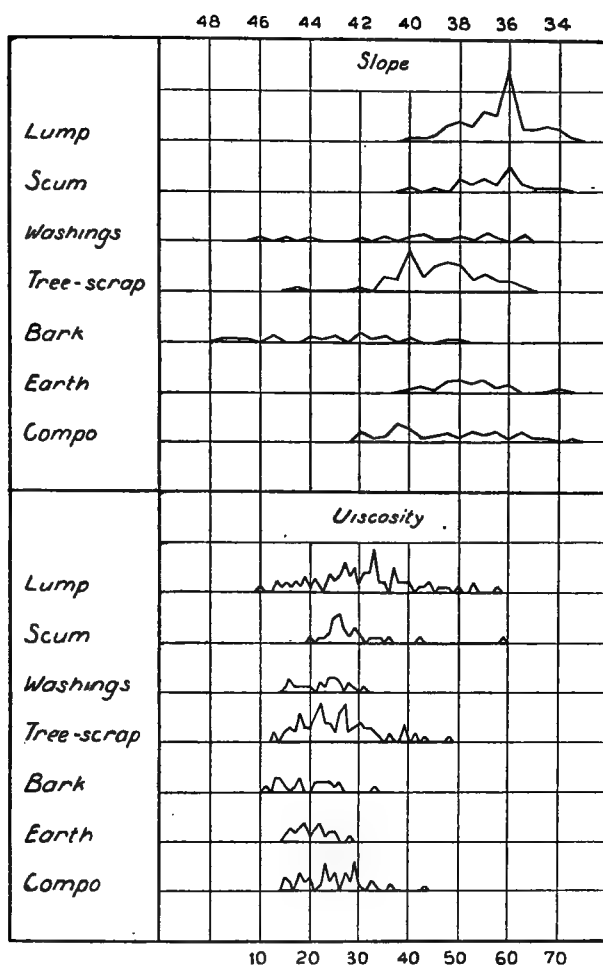


Fig. 9.

Slope and viscosity for a large number of samples of different grades.

somewhat quicker curing rubber, and the higher content of serum-substances in dried up latex (cupfilm etc.) may lead to the same result. In general, however, the rate of cure of all lower grades is surprisingly normal, and very abnormal figures such as are obtained by some methods of coagulation (for instance 180—240 minutes by the use of alum or sulphuric acid, see § 88 and 86) are never met with in the ordinary estate-output of lower grades.

The slope is a very valuable characteristic for classifying the lower grades of rubber, because to a certain degree this figure indicates the „purity” of the rubber; very rightly this property was called „type” by its author, and it is especially in the lower sorts that it stands for type or grade. From Fig. 9 it will be seen that in this respect crepe from lump and scum are the best. Scrap is noticeably inferior, while washwater and bark-rubber give very poor values.

Also in cases where a good rubber gives low figures for tensile strength because of included dirt, the slope gives a useful indication.

That the viscosity may vary a great deal, was to be expected after what has just been said about the other properties. The factors which influence both rate of cure and viscosity play a role in different combinations in the lower grades just as in the first quality product (see for instance § 185). To this may be added the decrease in tensile strength and slope, which can be accompanied by a lower viscosity. On the other hand a high viscosity combined with a low tensile strength gives sometimes an indication of a mechanical admixture of impurities (see § 39, 119 and 237).

The valuation of these types on the market is very variable. The colour, of course, makes it that these grades cannot be used in the manufacture of a number of articles, but if colour is not a consideration, these rubbers are often as good as first quality and, on account of their lower price, are readily taken up by some manufacturers. So bark-rubber, for instance, which contains particles of wood, but for the rest is prepared with care, can be used for certain articles, in which an admixture of particles of wood is no objection, just as well as first quality, and so at times there may be a demand on the market for cheap bark-rubber, provided it is good, while no interest is displayed in first quality rubber.

On the other hand, the widely divergent properties of these sorts do not add to an increased faith, while samples which have a tendency to tackiness are in all cases to be disapproved and should always be sold under a special mark.

The market judges these qualities practically exclusively on colour, and this is right to a certain degree, since the colour may be decisive for the use to which these types can be put. Rubber of good and bad inner properties may however be found just as well amongst the light, as amongst the almost black coloured samples, as will be clear from the examples given in the next paragraphs; and certainly the colour, in these grades, is not in the least an indication as to the properties after vulcanisation or the real strength and quality.

§ 176. Pre-coagulation.

When only a small quantity of acetic acid, for instance $\frac{1}{3}$ of the usual dose, is added to the latex, a clotty mass may separate after some time, which may amount to $\frac{1}{5}$ or $\frac{1}{4}$ of the total quantity of rubber, and which is called pre-coagulation. Without adding any acetic acid this may often also be effected by merely stirring, but then the pre-coagulation usually takes a longer time, perhaps several hours.

Partial coagulation was systematically applied in former years on some estates. The opinion was held—and up to a great extent it was right—that in this way the impurities were separated, so that from the rest of the latex the bulk of the rubber was obtained in an especially pure form. In fact the pre-coagulation contains, besides eventual particles of dirt, the largest part or all of the yellow colouring matter (see § 11), while the substances causing a violet discolouration (see § 12) are also for a great part carried along with it. From a normal latex, which on ordinary coagulation gives a pale yellow, nearly white crepe, the first clots obtained by pre-coagulation yield a deep yellow to saffron-yellow crepe, while the colour becomes more brown, approaching even a dark brown, in proportion as the coagulum has more tendency to violet discolouration by oxydation. To avoid this brown colour it used to be the custom on some estates to add bisulphite to the latex previous to pre-coagulation. The later clots, obtained by adding the remainder of the acetic acid to the „purified” latex, give a very pale crepe, which sometimes is even unnaturally white.

The properties of the first clots and of the rest of the rubber, obtained from one and the same latex, may be for instance:

	First clots	Rest
Tensile strength	1.35—1.40	1.45—1.50
Standard time of cure	90—95	105—120
Slope.	35—36	35—36 1/2
Viscosity	61—95	38—43
Coefficient of vulcanisation for standard curve	5.64 %	4.63 %
Nitrogen-content	0.64 %	0.47 %
Ash	0.48 %	0.25 %
Acetone-extract.	5.6 %	2.7 %

The „rest”, being the bulk of the rubber, has the same properties as the crepe prepared in the usual way from the same latex (which for the above examples were better than the average). The pre-coagulation (first clot) has a markedly lower tensile strength, vulcanises much faster, and has a higher viscosity, while the chemical composition shows clearly a higher percentage of accessory substances, so that indeed this rubber is less „pure”. If one takes further into account the strongly yellow or even brown colour, then it is obvious that crepe obtained by pre-coagulation will not be accepted as first grade; the external as well as the inner properties stamp this product as second grade. The idea, which some people hold, that the first clots from latex, and also the lump, contain the best that is in the latex, as cream is to milk, is absolutely wrong.

See O. DE VRIES, Arch. 1 (1917), 178 and 185, further O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 787; J. S. Ch. I. 38 (1919), 91, also I. R. J. 57 (1919), 1163.

In experiments by L. E. CAMPBELL (Bull. Ceyl. 27 (1916), pages 5, 9 and 28; Bull. Imp. Inst. 14 (1916), 554) the crepes obtained by fractional coagulation with acetic and hydrofluoric acid did not show the above indicated differences. This is, however, easily explained if the first clot forms 25 % or more of the total rubber, in which case its properties approach those of rubber coagulated as a whole. The first clot obtained from

spontaneous coagulation vulcanised somewhat quicker, but showed on the average the same tensile strength as the second and third clots.

Some samples of crepe of this type, prepared on different estates, gave the following figures:

Tensile strength	Standard time of cure	Slope	Viscosity
1.42	< 100	36½	65
1.35	> 100	38½	30½
1.26	85	36	44

therefore in all cases a greater rate of cure and mostly a higher viscosity than ordinary crepe; the tensile strength, however, in the first case is rather high.

On an estate, which used this method of partial coagulation to obtain a very white crepe from the bulk of the latex, we repeatedly tested crepe from both first clot and rest. The following figures are representative of these grades:

Type	% of total	Colour	Tensile strength	Standard time of cure	Slope	Viscosity
First clot	17—25	saffron-yellow	1.38	90—95	35½	65
Rest . .	75—83	pure white	1.47	105—110	35½	40

Since the rest of the rubber, after pre-coagulation, in spite of its very white colour does not fetch a correspondingly better price on the market which makes up for the loss in the pre-coagulation, this method of preparation proved unprofitable and is therefore seldom applied.

On some estates there is a kind of natural pre-coagulation, namely the clotting of the latex which occurs on some days, and which is kept apart when straining the latex and sold on the market as a special mark of lump-rubber.

A knowledge of the properties of rubber obtained by precoagulation may be, however, of importance to explain the properties of some types of lump-rubber, as well as to judge crepe with brown or violet streaks formed by premature coagulation (see § 167).

Another way of „purifying” the latex by partial coagulation, used on estates in former years, was a kind of defecation, in which the latex was heated slowly: on stirring, a froth or scum-like partial coagulate was formed, which enclosed dirt and colouring matter, leaving the rest of the latex to give a very light coloured rubber. The properties of the so formed pre-coagulation have not been investigated; probably they were poor. The method was abandoned for the same reasons as the above; several modifications of it are mentioned in § 100.

For descriptions of this method and the apparatus used for it see for instance E. DU BOIS, *Teysm.* 23 (1912), 237 and A. J. ULTÉE, *Rubb. Rec.* 1914, page 391.

§ 177. Lump.

Under the term „lump” are generally designated all sorts of clots or lumps which remain on the sieves when the latex is strained in the factory. Often the pails contain a large clump of coagulated rubber, which is taken out by hand, sometimes squeezed to press the latex out and kept apart; on the sieves smaller clots are retained, which stick together and are rubbed away, as they clog the holes of the sieve. Of course, all kind of impurities may be incorporated with this lump, such as fallen leaves, pieces of bark cut away in tapping, insects which found an untimely death in the creamy latex etc., and lump-rubber therefore is generally somewhat dirty, though much less so than most of the other grades to be treated in the next paragraphs.

The coagulated pieces may have been formed in many different ways and therefore may have very different properties. The film which forms on the wall of a cup, for instance on the spot where the latex drips in, is simply caused by the drying up of the latex in the air and may be considered as closely related to scrap or cupfilm (see § 180).

Its properties will be those of rubber obtained by total evaporation (see § 102).

Somewhat similar is the membrane formed on the surface of the latex by evaporation in the cup, especially during the dry monsoon.

The clots, formed out of these thin films when the latex is poured from the cup, may further increase in size during transport owing to premature coagulation.

Still other clumps are formed by total or almost total coagulation in some cups, as the latex of some trees may have a special tendency to rapid spontaneous coagulation. Lumps of this origin therefore show the properties of ordinary, spontaneously coagulated rubber.

Further there is the clotting or the beginning of curdling which is a true kind of partial coagulation, although in some pails, which on straining are found to contain almost a porridge-like mass, so much of the rubber may have coagulated that one should rather speak of „coagulation” than of „partial coagulation”.

Concerning the way in which these different types of „lump” are formed and the factors that influence them, our knowledge is still lacking in many points. The anti-coagulants, which may be used to prevent lump-formation, are treated in Chapter III.

Figures for 90 samples of lump-crepe are reviewed in the following table (compare Fig. 8 and 9).

	Mean	Limits
Tensile strength.	1.33	1.07—1.50
Standard time of cure. .	104 $\frac{1}{2}$	7—130
Slope	37.3	33 $\frac{1}{2}$ —40
Viscosity	30.5	10—58

Among these, therefore, very good types are found, which are only slightly inferior to first quality crepe; but there are also poor ones, which very nearly approach the inferior grades.

So for example:

	Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Good types	Light brown	1.45	110	36	33
	Yellow brown	1.44	100	37	37½
	Brown	1.40	115	33½	39
Poor types	Dark brown	1.24	90	38½	20
	Yellow brown	1.26	130	38	20½
	Brown	1.24	120	39	17

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. 27 (1918), 352) give figures for 9 samples of lump-crepe, which show a tensile strength of 1.29 to 1.50 (against ordinary crepe 1.30, and smoked sheet 1.46), whilst the time of cure was 2¼ to 3¼ hours (against 3¼ and 2¾ respectively).

A low tensile strength may naturally be due to particles of dirt enclosed in the coagulum; if the other properties are good, especially the viscosity, it is worth while to wash and recrepe the sample. For example a rather thick crepe from lump gave us on testing a low figure for tensile strength, but a high viscosity: on recrepeing a much higher and perfectly normal figure for tensile strength was obtained, proving that the rubber itself was good, but contaminated by dirt (compare § 237 and Fig. 27):

	Tensile strength	Standard time of cure	Slope	Viscosity
Sample as received. .	1.15	> 100	37½	47
After rewashing and crepeing.	1.31	> 100	36	47

Some samples of lump-crepe clearly show in their properties that they were formed by partial coagulation, for instance:

Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Brown	1.27	95 min.	36	36 $\frac{1}{2}$
Yellow brown . . .	1.22	95 "	35 $\frac{1}{2}$	36 $\frac{1}{2}$

The — for thin lump-crepe — fairly large rate of cure and high viscosity, coupled with rather low tensile strength, point in the direction of pre-coagulation; on further going into the matter on the estate it was found that these samples of lump for the greater part had indeed been formed by partial coagulation.

The colour of lump-rubber has a wide range, running from a dark yellow or yellowish brown through all the tints of yellowish and reddish brown to a very black brown. This, of course, depends for the greater part upon the degree of oxydation that took place during preparation.

§ 178. Scum.

When the latex is poured through the sieves into the receiving tank, and transferred to the coagulating tank or pans, a rather voluminous scum is formed, which has to be removed before coagulation sets in, because the surface of the sheets would show the marks of such bubbles, and in crepe light brown streaks might appear.

If the latex is skimmed before the addition of acetic acid, one obtains, even when carefully pouring back all the latex which collects from this scum so that only the scum remains, a very good crepe which is not inferior in properties to first quality crepe. The exterior is, however, often slightly less attractive, somewhat darker and striped; but from the view-point of the inner properties there should be no reason why this crepe should not be added to the „off colour first quality”.

It is a somewhat different matter if one skims the latex after the addition of acetic acid; the scum is then generally clotty, and assumes more or less the character of pre-coagulation that is of a second grade.

Especially in later years, now that estates have taken more and more to producing only a small number of grades, the scum is seldom worked separately; if one, however, desires to keep this sort apart, then it would be well to keep in mind the above mentioned difference and to work only the scum that is collected before the addition of acetic acid into an off coloured crepe, whilst the scum mixed with pre-coagulation is added to the compo or lump.

We found the following values for the inner properties of 30 samples from different estates:

	Mean	Limits
Tensile strength	1.34	1.24—1.42
Standard time of cure	112½	85—135
Slope.	36.8	34—40
Viscosity.	28.5	20—59

It is not known in how far these samples comprise scum collected before or after the addition of acetic acid.

It will be seen that the average is very good and differs little from the average values of first quality crepe; some of the samples gave results which were not so good.

The colour of crepe from scum may vary from the whitish yellow colour of ordinary crepe to brown, but it is seldom so dark as in the other second grades.

§ 179. Washings.

A diluted latex from washings is obtained from several sources. In the first place, when the cups are washed with water in the field (see § 39), every coolie, besides his pail of „pure” latex, brings in a pail with washings, so that a large volume of this diluted, often dirty latex is obtained, from which the rubber is collected by adding acetic acid (often in the form of undiluted acid).

Further the pails have to be cleaned, and a remnant of latex is generally left in them, when pouring their contents

onto the sieves, so as to keep the sand and heavy dirt in the pails. Further the mixing tank and several other vessels furnish a certain amount of washings, whilst several remnants of latex, suspected of not being too clean, may also be added. In this way a rather large volume of a diluted, and often very much diluted, latex is daily obtained, from which the rubber is coagulated by adding acid.

For some 25 samples of this type we found the following figures (compare Fig. 8 and 9):

	Mean	Limits
Tensile strength	1.27	1.06—1.45
Standard time of cure. . .	118	95—145
Slope	39.1	35½—46
Viscosity.	22.6	15—31

i.e. properties which depart somewhat from those of first quality crepe or smoked sheet, but for second grade rubber are quite satisfactory.

In § 64 we stated that diluting the latex (with pure water) has a less harmful effect on the rubber than is often supposed, but in the washings and rinsings the latex is often diluted to such an extent that from this cause alone the rubber will be somewhat inferior (small decrease in tensile strength, large decrease in rate of cure). To this factor has to be added the danger of dirt and infection, which is great when the cups are rinsed in the field, because in some cases, in spite of orders, muddy water from the ditches will be used. One must, however, also remember that even if the cups are cleaned with pure water in the factory, those which stood on the soil next to the tree are dirty outside, so that dirt and soil may get into these washings. It is no wonder then that the worst types of rubber by far are found amongst crepes from washings, and that some of these types quickly become tacky and give low figures. For instance:

Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Brownish gray. . .	0.80	100	50	7
" " . .	1.03	100	51	7 $\frac{1}{2}$
Dark brown. . .	0.93	110	53 $\frac{1}{2}$	7

These are values not often met with even in earth- or bark-rubber; tensile strength as well as slope and viscosity are abnormally poor, as is also clearly seen from Fig. 8 and 9.

There are, however, other samples which were sent in for testing under the name of „washings”, but which in regard to inner properties were little short of first quality crepe. For instance:

Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Brown	1.36	< 125	37	26 $\frac{1}{2}$
Light brown. . .	1.42	125	36	25
Yellow brown . .	1.42	125	35 $\frac{1}{2}$	24

These samples clearly show the character of having been coagulated from moderately diluted latex: tensile strength and slope are normal and up to the average for crepe, the rate of cure and viscosity are somewhat smaller than the normal figures. In these samples the rinsing of the cups or pails was apparently done with as little water as possible. In § 70 we have already mentioned that such rinsings, provided the water is pure and contains no dirt, can be profitably used for diluting the latex to standard rubber-content.

On various estates these comparatively pure rinsings are collected separately and worked into a sheet, which, to be sure, does not look as well as first quality sheet, but so far as external appearance goes may be classified satisfactorily under „off quality”.

For some samples of this type we found the following figures:

	Mean	Limits
Tensile strength. . . .	1.30	1.24—1.38
Standard time of cure. .	108	90—145
Slope.	38	35—39
Viscosity	28 *	17 $\frac{1}{2}$ —38

Rubber from washings belongs to the types which on many estates are not kept separate. One would wish that the dirty and strongly diluted washwater, from which a very inferior rubber is obtained, were not used at all, but thrown into the gutter; the pure rinsings then might be added to the latex, while the somewhat impure and not too dilute rinsings might be coagulated and worked with the scrap and compo.

From the standpoint of economy this also deserves consideration, since the very dilute washwater uses up a proportionately large dose of acetic acid in coagulation and makes the cost on this head unnecessarily high.

That the colour of a type of rubber, which varies so widely in properties as rubber from washings, varies very largely, goes without saying. Among them rubbers are to be found of a pale yellow colour, while others show a brownish black, and all possible shades between these are met with; amongst them sometimes a peculiar red or reddish brown nuance may be observed, mostly due to the use of muddy water or water containing iron.

§ 180. Cupfilm.

The estates, which tap „dry” and do not have the cups brought into the factory, collect the latex which adhered to the cups and dried up to a film on the following day under the name of „cupfilm”.

Usually this rubber is added to the tree-scrap; some samples, which were collected and tested separately, gave the following figures.

Estate	Type	Colour	Tensile strength	Standard time of cure	Slope	Viscosity
I.	cupfilm washwater	gray brown	1.33	< 90	37½	40
		brown	1.35	110	36	26 ½
II.	cupfilm (3 samples)	dark brown	1.05	80	38	19

For comparison the values for washwater from one of these estates, obtained by rinsing the cups, are added. The cupfilm has, as one would expect for a rubber from dried up latex (see § 102), a quicker cure and a higher viscosity, but in properties it fits in very well with crepe from tree-scrap.

A closer comparison between this grade and tree-scrap, which is also a dried up latex, but perhaps with loss of serum-substances by absorption in the wood, might be interesting in many respects.

§ 181. Tree-scrap.

After tapping the latex flows slowly down the somewhat sloping tapping cut, and then down the vertical channel and the spout into the cup. Sooner or later the latex on the cut and in the channel dries up, and gets so thick, that the further flow is retarded; and this remnant of latex further dries on the tree. Some estates collect this tree-scrap or scrap, as it is often simply called, in the afternoon by special gangs of coolies, so as to machine it as quickly as possible, so that oxydation does not proceed and the colour remains lighter; but this has the disadvantage that the latex-vessels are partly reopened, so that drops of latex appear here and there on the tapping cut, and a fresh quantity of scrap is formed which does not form a continuous long strip, but separate patches, and remains on the strips of wood which are scaled off during tapping the next day, thus augmenting the percentage of bark-rubber.

See for instance DE RYCKMAN DE BETZ, Rubber Rec. 1914 page 320; also C. Gp. 1915, page 8719.

Most estates have the tree-scrap collected next day, by the tapper, who winds off the strip of rubber before reopening the tapping cut, and brings the strips of rubber, rolled together into a ball, to the factory with his pail of latex.

The figures obtained in our testing of 90 samples of tree-scrap from different estates, received in the course of four years, are shown in Fig. 8 and 9. They may be summarised as follows:

	Mean	Limits
Tensile strength	1.25	1.04—1.46
Standard time of cure	105	70—135
Slope.	38.8	35½—44½
Viscosity	25.7	13—48

These values, as is also apparent from Fig. 8 and 9, vary greatly. Among the scrap-crepes very good types of rubber are found, which are only slightly inferior to the first quality; but other samples are very inferior.

As examples we add here some figures for different samples:

	Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Good types	Black brown	1.37	< 90	38	26
	Light brown	1.40	< 120	37	27
	" "	1.42	110	36½	32½
Inferior types	Yellow brown	1.20	> 110	41	20½
	Black brown	1.10	> 125	42	15
	" "	1.24	115	40	16

Probably the method of preparation is for a good deal the cause of such differences; quick and cool working will in all cases be favourable, whilst prolonged keeping, fermentation and sunlight must be looked upon as unfavourable. Positive data to prove this, and to show the exact influence of each separate factor, are still wanting.

A low tensile strength in this grade may also be due sometimes to the mechanical admixture of particles of dirt and wood; in the last three samples of the above table, however, the high figure for slope and the low viscosity mark the rubber clearly as inferior. From Fig. 9, in fact, it appears that especially in slope and viscosity the samples of scrap-crepe deviate appreciably from lump-crepe (and from first grade rubber).

On some estates the tree-scrap was or is sorted into two or three colours; ordinarily a decided difference in inner properties is found between these in testing. For example :

Estate	Colour	Tensile strength	Standard time of cure	Slope	Viscosity	
I	a	Brown	1.33	< 115	38	31
	b	Dark brown	1.12	110	39	29
II	a	Light brown	1.39	> 95	38	39
	b	Dark brown	1.35	< 110	38 1/2	34 1/2
III	a	Brown	1.35	125	36	48
	b	Dark brown	1.25	90	37	41
	c	” ”	1.27	< 110	39	39

See O. DE VRIES and H. J. HELLENDORRN, Arch. 1 (1917), 224.

In all three cases there is a marked difference in tensile strength, slope and viscosity.

Some ten samples which were sent in under the name of „black scrap”, gave the following data on testing:

	Mean	Limits
Tensile strength	1.23	1.11—1.35
Time of cure	106½	85—130
Slope	40	38—42
Viscosity	25	15—39

therefore a decidedly higher (worse) slope than the average figure given above, while the viscosity and the tensile strength were also somewhat less.

A. J. ULTÉE (Arch. 3 (1919), 412 and 417) found, for a series of samples of pale and dark tree-scrap from one estate, the average viscosity to be 113 against 97, and the ash-content 0.51 against 0.68 %.

The average time of cure for scrap-rubber (105 min.) is a little less than for normal crepe, but is quite similar to that for crepe made from undiluted latex. Since scrap is produced by the drying up of the latex, one would expect that all the serum-constituents were taken up and that the vulcanisation would be quicker, as for rubber obtained by evaporation (see § 102). This, however, is not the case. This has been explained by assuming that the serum-constituents are absorbed by the porous bark of the tapping cut; in fact scrap does not feel greasy like rubber from dried up latex, which contains all the serum-constituents. This explanation will, however, have to be proved more explicitly, and one cannot say that the properties and the formation of tree-scrap, especially the rather rapid coagulation on the cut, are wholly cleared up.

B. J. EATON (J. S. Ch. I. 36 (1917), 1224; Bull. F. M. S. No. 27 (1918), 353) found the rate of cure of scrap-crepe intermediate, and generally similar to that of sheet. He explains this by the absorbent action of the bark, as he found that rubber dried up on a porous plate (*ibid.* 1224 and 79) cured in 2¼ hours, whilst drying up on a glass plate (in another experiment however) gave rubber which cured in 1¼ hours.

On the influence of Hevea-bark extract on latex see G. VERNET, Bull. Mars. 1 (1919), 111, and § 92, page 196; whether substances from the content of other cells than the latex vessels, that are cut open during tapping, have an influence on the formation of tree-scrap, is not yet known.

§ 182. Bark-rubber.

Every day, when tapping, a small strip of bark is removed to open the latex vessels; and these scales or shavings are collected and brought to the factory, in the first place as a check that the tappers do not remove too much bark, and in the second place to extract some rubber from it. The pieces of bark are simply fed into one of the crepeing-machines, which grinds them to a pulp from which the fine particles of wood are washed away with the water, whilst the rubber gradually sticks together and at last forms a coherent crepe.

This rubber consists of pieces of tree-scrap which were left on the tapping cut, because the tapper generally has no time to remove every small piece of scrap and make the cut absolutely clean before he cuts a thin layer away.

From the wood (or better bark) itself practically no rubber is obtained; the amount of rubber in the latex cells is too small to be collected by crepeing the bark, and if one carefully picks out every piece of tree-scrap from the parings, no bark-rubber at all is obtained on crepeing.

On some estates, where labour is cheap, the bark is only picked by hand and not ground on the machines, which means a sparing of the rolls and a better, cleaner type of rubber. Mostly, however, the milling of the whole lot of parings is easier, cheaper and quicker.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. 27 (1918), 351) indicate that ordinary bark, as received in most factories, contains some 15 % of its weight of rubber.

Shavings, carefully picked free from tree-scrap, yielded us less than $\frac{1}{2}$ % in weight of rubber, and if picked absolutely clean, probably no rubber at all would be obtained on milling, though the wood may contain some dried up latex, which might be gathered in other ways (extraction or so).

Strictly speaking, therefore, bark-rubber is simply tree-scrap, contaminated by small particles of wood which were not washed away, and drenched in bark-extract, which gives a very dark colour to this crepe.

Still the properties of bark-rubber are very varying and are not nearly so good as those of tree-scrap. For the

tensile strength, which is deteriorated owing to the presence of particles of bark, this is easy to understand; whether the changes in slope and viscosity are caused either by the bark-extract or by other causes, is as yet unknown.

For 25 samples from different estates we found (see Fig. 8 and 9):

	Mean	Limits
Tensile strength	1.08	0.82—1.36
Standard time of cure . . .	111	90—140
Slope.	42.9	38—47 $\frac{1}{2}$
Viscosity	19.5	11—33

From these figures it is clear that the tensile strength is nearly always low, while the rate of cure and viscosity correspond with those of tree-scrap. The slope is, for various samples, noticeably less.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. 27 (1918), 355) mention figures for eight samples of bark-rubber, showing a tensile strength of 0.78 to 1.48 and a time of cure of 2 $\frac{1}{4}$ to 3 hours.

The ash-content of bark-crepe is generally higher than that of the better grades, and may reach 1 % and more; this, of course, is greatly influenced by the amount of bark and sand the rubber contains.

A. J. ULTÉE (Arch. 3 (1919), 416 and 417) found 0.66 to 1.03 % of ash in a series of samples of bark-rubber; we found in one sample even 1.38 % which on washing and recrepeing only decreased to 1.36 %.

As the treatment of several diseases includes painting of the freshly tapped surface either with tar or disinfectants, the tree-scrap in such cases may get contaminated by these substances; it is then generally left on the shavings and worked into the bark-rubber. Sometimes the chemical analysis of the rubber, especially the acetone-extract, may clearly show the presence of foreign substances, but in other cases the treatment appears not to deteriorate the rubber.

As an example we may add the following figures:

	As received		After recrepeing	
	Acetone-extract	Ash	Acetone-extract	Ash
Bark-crepe, no tar . . .	2.7	1.38	2.35	1.36
" " with tar . . .	3.6	1.20	3.1	1.18
" " " " . . .	5.7	1.96	5.4	1.95

§ 183. Earth-rubber.

By some accident or mistake (for instance a piece of dirt in the tapping-channel which deflects the stream of latex) latex may flow onto the ground instead of into the cup; a cup may be turned over, or latex may get onto the earth at the foot of the tree in other ways. This latex then dries up or coagulates, and is collected either every day (during tapping) or at regular intervals. This earth-rubber is ipso facto a dirty rubber, as it is picked from the soil, and one can never completely remove all the earth particles even by careful washing. Further, if it is not collected regularly at short intervals, tackiness may develop either by infection or by the effect of sunlight. Many samples of earth-rubber become tacky on keeping, and with low rubber prices it is soon doubtful whether it is remunerative to gather and work this kind of rubber or not.

For 28 samples of earth-rubber from different estates we found the following figures (compare Fig. 8 and 9):

	Mean	Limits
Tensile strength	1.26	1.06—1.38
Standard time of cure . . .	97½	70—130
Slope.	37.6	34—40
Viscosity	20.1	15—28

Therefore as a rule a low tensile strength and often a low viscosity is found, accompanied by a comparatively normal rate of cure and slope. Naturally, 28 samples do not give a complete picture of this type, especially because the evidently poor samples of earth-rubber are perhaps not so often sent to the laboratory for testing, which, to be sure, would be wasted on them.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F.M.S. 27 (1918), 356) found the tensile strength for five samples of crepe from earth-scrap between 0.88 and 1.27, and the time of cure $2\frac{3}{4}$ to $3\frac{1}{2}$ hours. They explain the „normal“ rate of cure by an absorption of serum-substances by the soil.

The ash-content of earth-rubber may be, of course, quite high, according to the amount of soil-particles included. Figures such as 2% and more are no exception.

A. J. ULTÉE (Arch. 3 (1919), 416) found an ash-content of 0.96 to 2.80% in a series of samples from two estates.

It is remarkable that this rubber, which often remains for days in the form of wet lumps, does not show the increased rate of cure and further characteristics of matured rubber. The absorption of serum-substances by the soil (see above) would seem no sufficient explanation, as enough serum must remain absorbed by the rubber to give maturation.

That tacky samples of earth-crepe may deteriorate markedly on keeping needs no proof. Some figures may give an idea of this deterioration.

	Tensile strength	Standard time of cure	Slope	Viscosity
I. Earth-rubber, tested directly	1.21	130	$37\frac{1}{2}$	22
Same, after two years	0.85	135	—	$11\frac{1}{2}$
II. Earth-rubber, tested directly	1.21	125	38	$21\frac{1}{2}$
Same, after two years	0.88	140	—	$8\frac{1}{2}$
III. Earth-rubber, tested directly	1.14	115	$37\frac{1}{2}$	$23\frac{1}{2}$
Same, after $1\frac{1}{2}$ year.	0.47	120	—	11

§ 184. Compo.

Compound crepe or compo is the name given to the combinations of different lower grades into one type.

Strictly speaking, nearly all of the lower grade crepes are compound, as generally some kind of rubber or other is added to the bulk of one type: part of the scum or perhaps the washing to the lump, dark scrap to the earth, films dried up on the walls of the coagulating tanks or pans, and remnants of rubber from corners of coagulating tanks to the lump or scrap-crepe, etc.

With the intention of diminishing the number of grades put on the market, and at the same time of producing a brown crepe of more uniform properties, many estates have taken to combining their lower grades. Sometimes the yellow and light brown types are machined together to a light brown compo A or No. 1, whilst the dark rubber gives the second grade compo. Other estates produce one type of compo, including all grades down to tree-scrap, or (if a very good and strong washing machine is available) even bark. Earth-rubber, with deteriorated remnants of rubber from other sources (tacky rubber and so on) is always kept and sold separately. If one is so fortunate as to have a good washing machine (for instance of the Universal type), a very clean rubber of good quality may be produced which is very uniform, due probably to the mixing and averaging up of all grades. For samples of one estate we found:

	Tensile strength	Standard time of cure	Slope	Viscosity
May	1.43	110	36	—
October 1	1.39	> 105	37 1/2	31
" 2	1.38	100	37	32
" 3	1.34	110	37	31
" 4	1.31	110	37 1/2	30 1/2
" 5	1.35	110	37	30 1/2

These figures are very uniform, and excellent for a mixture of lower grades.

A series of six samples from another estate gave the following figures:

Tensile strength	Standard time of cure	Slope	Viscosity
1.27	85—90	40	22½ — 28½

These figures are also very satisfactory and show a uniform rate of cure.

Some 45 samples of compo from different estates gave the following figures (see also Fig. 8 and 9):

	Mean	Limits
Tensile strength	1.31	1.20 — 1.42
Time of cure	94	80 — 120
Slope	38.4	33½ — 42
Viscosity	24.4	15 — 43

As we said above, other estates mix only some of the different grades; for instance, scum, lump and white scrap into one and black scrap with bark-rubber into a second compo.

In general it may be assumed that the properties of such mixtures show values in between the properties of the types mixed therein. For instance:

	Tensile strength	Standard time of cure	Slope	Viscosity
I. Scrap	1.31	> 115	38½	30
Compo (scrap + earth)	1.35	> 120	38	24½
Earth	1.21	< 130	37½	22
II. Lump	1.44	100	37	37½
Compo (lump + washwater)	1.42	< 110	37½	20*
Washwater	1.28	135	38	12

One must, however, in compounding such mixtures, be careful not to spoil the good rubber by mixing it with inferior types. The following figures for mixtures made on an estate are very instructive in this respect:

	Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Lump and wash-water . . .	brown	1.22	< 115	43½	20
Scrap and earth	dark brown	1.37	140	38½	27

See O. DE VRIES and H. J. HELLENDORF; Arch. 1 (1917), 226.

Evidently it was thought that the first mixture with its brown colour was the better of the two; but — probably because of the bad properties of the washwater-rubber — the first mixture is far inferior in tensile strength, slope and viscosity. It would, without a doubt, have been better in this case to mix the lump with the scrap, and the wash-water with the earth-rubber.

In how far the mixing of the lower grades into „compo-crepe” is profitable, depends upon the market-conditions, and especially upon the prices paid for the lighter and the darker brown coloured sorts. Generally, the colour and exterior of the „compo” is good, and if well executed the procedure, as far as data are available, seems profitable.

From a standpoint of preparation and properties the making of compo deserves every recommendation, since fewer separate grades are obtained and these with more uniform properties, while the Universal or other washing machine, necessary for this method of preparation, can be nothing but beneficial to the quality of the rubber.

§ 185. Some remarks on the preparation of the lower grades.

Some observations, which relate especially to the preparation of lower grades, may be added here.

1). *Keeping before rolling.*

That changes may take place in the rubber by keeping these grades before machining, is self-evident. Rolling directly or on the following day gives the differences in rate of cure already often discussed (see § 117 and 135), for instance:

	Colour	Tensile strength	Standard time of cure	Slope	Viscosity
Lump, creped the same day . . .	yellow	1.40	120	34½	38
Lump, creped the following day .	greyish yellow	1.42	95	35	37

For the same reason thick lump or scrap-crepes, as a rule, vulcanise more quickly than ordinary thin crepes.

Complete maturation may occur on long keeping. For instance a lump-rubber, which could not be worked in time because the crepeing-machine had not arrived, and which remained for several months in the form of lumps or kneaded balls, gave the following figures, in comparison with freshly rolled lump from the same estate:

	Tensile strength	Standard time of cure	Slope	Viscosity
Lump, rolled when fresh	1.28	120	36	18
Lump, kept for a long time. . . .	1.30	70	35½	28½

i. e. the ordinary changes caused by maturation.

See O. DE VRIES, Arch. 2 (1918), 231 and 240.

In keeping the lower grades there are, however, still other factors which deserve attention, such as deterioration when the rubber was infected, of which we gave a few examples in § 183. Further, when tree-scrap or bark are kept in a heap for the night before rolling, the moist mass may

get considerably heated, which, of course, is far from beneficial to the rubber. Keeping under water or soaking in dilute bisulphite is used in such cases, see below.

Data concerning the influence of such factors on the properties of the rubber are, however, still very scarce. Rolling as soon as possible after collection is in all cases to be recommended to avoid deterioration; it has the further advantage that less oxydation takes place, and the colour therefore remains lighter.

2). *Soaking the lower grades.*

Though in general it is better to machine the lower grades as soon as possible, the arrangement of the work in the factory does not always allow of treating the lower grades on the day they are brought into the factory. Some estates even prefer to keep the bark-shavings one night under water, so as to weaken them and diminish the wear of the rolls; others dry the parings as much as possible and have the bark crushed by stamping.

The other grades (lump, scrap, etc.) are also often kept for one night, and to prevent heating, fermentation and oxydation, they have to be kept in water; to keep the colour as light as possible, a dilute solution of bisulphite (say $\frac{1}{2}\%$) is often used, or the serum from the same morning.

A bath of bisulphite, acidified with sulphuric acid, is also recommended for this purpose; whether this is harmless to rubber, remains to be investigated.

See the patent description for soaking in a 1 to 3% solution of a bisulphite, hydrosulphite or sulphite, to which 0.1 to 0.5% of sulphuric acid may be added, I. R. J. 55 (1918), 268.

B. J. EATON (Agric. Bull. F. M. S. 7 (1919), 225) warned against soaking in sulphuric acid (compare § 86), but the above bath is intended to contain only sulphurous acid and no free sulphuric acid; its effect is still unknown.

3). *Crepeing.*

In § 120 it has been already mentioned that the lower grades of rubber are more sensitive to heat during rolling than good first quality crepe.

The following data give an idea of the effect of heating during machining of a mixture of lump, scrap and washings.

	Tensile strength	Standard time of cure	Slope	Viscosity
Rolled as usual. . . .	1.40	110	35	23 1/2
„ warm	1.34	< 120	37 1/2	11

Thus a marked deterioration in all properties by a treatment under which first quality only suffered a slight decrease in viscosity whilst the other properties remained unchanged.

See O. DE VRIES and H. J. HELLENDORRN, Arch. 2 (1918), 549 and 559.

This point deserves attention, since one is inclined to pass the lower grades through the rolls rather often, so as to obtain an even coloured crepe without stripes. It may be assumed that the washing and kneading in a Universal or similar washing-machine, followed by short crepeing, is far more favourable to the inner properties than rolling many times, by which the crepe often becomes somewhat heated, while by the former method one also more easily obtains an even colour.

A. J. ULTÉE (Arch. 3 (1919), 417) found the viscosity of bark- and earth-rubber to be higher when a Universal washer is used; for instance for bark 112 against 104, for earth-rubber 103 against 96. At the same time the ash-content was lower, showing that the rubber was better cleaned in the Universal machine (0.78 against 0.82 % for bark, 1.46 against 2.22 % for earth).

CHAPTER XIV.

THE BRAZILIAN METHOD OF PREPARATION.

The Brazilian method of coagulating the latex by hot smoke and preparing the rubber in the form of smoked balls deserves special attention, not only as the oldest way of preparing superior rubber, but also because this rubber commands a higher price in the market despite the fact that it contains 10 % and more of moisture and has to be washed and dried before use.

Whether this higher price is due to its special merits—be it in general, or for special purposes—or whether this demand arises from other causes, still forms a point of discussion, about which published data do not allow a conclusion, and into which we will not enter (see however some remarks in § 105).

A closer study of the properties of rubber prepared after the Brazilian method and of the characteristics of this method of preparation may be regarded as important in many respects.

§ 186. Composition and properties of Brazilian rubber.

As a comparison with the figures given for plantation-rubber in general, and for the rubber prepared after the Brazilian method to be described in this chapter, we will first review shortly some of the data on Brazilian rubber found in literature.

For the *moisture-content*, or better the loss on washing, divergent figures of course are found, as this figure may vary owing to so many factors, including the age of the balls, the evaporation from outer and inner layers and so on. The figures mostly lie between 10 and 20 %.

The washed (creped) and air-dried rubber still contains some moisture, which may vary from 0.2—1 %.

The *composition* of the washed and dried rubber may be taken to be approximately:

resin	3 %
protein	2—3 %
ash	0.3 %
water-extract	0.5 %

The chemical composition of Fine Hard Para is therefore approximately the same as that of plantation crepe or sheet. The watery extract is the same as that of sheet; the acidity is found to be a little lower than that of sheet (see § 244). This should be sufficient to prove that Fine Hard Para does not contain all or even most of the serum-substances from latex, as is so often supposed. Though descriptions of the method of preparation in Brazil are mostly very reticent on this point, some authors distinctly state that a great part of the serum sweats out from the fresh coagulum, whilst it is well known that the balls, when cut open, often lose a fairly large amount of „water” (better serum) enclosed in pockets, which may spout out with force. But about the amount of serum-substances removed in this way during preparation in Brazil no data are available. As we shall see in § 188 the balls prepared in Java sweat out more than half of the serum-substances.

P. CIBOT (J.d'A.T. 3 (1903), 36; 5 (1905), 124) from his experience in Bolivia mentions that in making „planchas” (small slabs from one day's product, in contrast with the large balls or bolachas) during coagulation and smoking 7% of the weight of latex is lost, whilst in four days the loss in weight, both by dripping and evaporation, amounts to 33% of the weight of latex. A large ball of 75 K.G., from 23 days production, weighed, freshly prepared, 67½ % of the latex and after 8 days 61 %; but though sweating is mentioned as causing part of the loss in both cases, figures for the separate loss by sweating and/or evaporation are not given.

See further V. CAYLA (J.d'A.T. 13 (1913), 233) and H.C. PEARSON (The Rubber country of the Amazon, page 70), who describes the sweating out of „a great deal of water”.

As regards the *properties after vulcanisation*, most investigators, who have compared plantation-rubber with

Brazilian balls, found that the former may have—but not always—the same or superior qualities, and that ball-rubber, taken as a whole, is more uniform (especially in rate of cure) than plantation Hevea rubber from different sources.

The *rate of cure* of Fine Hard Para is mostly given as very near the values for smoked sheet.

B. J. EATON and J. GRANTHAM (Agric. Bull. F. M. S. 3 (1915), 194, and Bull. F. M. S. No. 27, 364) found the rate of cure very similar to that of smoked sheet.

The coefficients of vulcanisation for a fixed cure given in Comm. Delft V, page 170 are also near the average for smoked sheet.

An explanation of this figure is not yet possible. Several factors come into account, such as the age of the trees, the quantity of serum-substances left in the rubber, the influence of coagulation by heat, the influence of smoke-constituents, maturing of the balls etc. These factors will be discussed in § 190, in connection with our own experiments; but of course the influence of each of these factors in actual preparation in Brazil can only be studied by comparative tests on the spot.

The most striking fact in the rate of cure of Brazilian balls is that, though containing enough moisture to mature, they do not show the large rate of cure of matured rubber.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 364) explained this „normal” rate of cure of Fine Hard Para by two counteracting factors, viz. the presence of all serum-substances, which accelerate, and the chemical or antiseptic action of the smoke-products and the heat, as retarding agents. The first supposition cannot serve, as the balls do not contain all or most of the serum-substances (see above and § 188); but perhaps the smoke-constituents, retarding agents in themselves and at the same time antiseptics, may at least to some extent prevent maturation, and so keep the balls at the „normal” rate of cure. Compare § 190.

P. CIBOT (J.d'A.T. 3 (1903), 36) draws special attention to the fact that the smoked coagulum on the balls never develops the putrid smell of unsmoked coagulum on keeping. But from this it may not be concluded that no maturation takes place (see § 189).

Uniformity in rate of cure is perhaps now the principal point on which superiority is claimed for Brazilian rubber. An exact judgment, of course, can only be based on a large quantity of figures, from which the degree of variability could be calculated. Published data are not sufficient for such a strict comparison, but, so far as they go, they certainly point to a lesser variability in Brazilian rubber.

See for instance EATON c.s. (l.c.), who found the rate of cure in a number of samples to vary only from $2\frac{1}{2}$ to $3\frac{1}{4}$ hours, against $1\frac{1}{2}$ — $3\frac{1}{2}$ for smoked sheet and 2 — $3\frac{3}{4}$ for first latex crepe. See further Comm. Delft V, page 170, where nine samples of Fine Hard Para showed coefficients of vulcanisation of 2.67 to 3.81, when subjected to the same cure.

In this connexion it should however be remarked that the balls, prepared after the Brazilian method on estates in Java, all have a much greater (almost twice as great) rate of cure, which comes very near that of matured rubber. There is therefore in the Brazilian method of preparation at least one factor, which — being different in Brazil and in Java — may give large differences in rate of cure.

The first point on which research on this question will have to bear is whether the uniformity in Brazilian balls is perhaps partly explained by the condition and age of the trees and the method of tapping in Brazil, by which possibly a latex of more constant composition is obtained than on plantations.

Apart from this possibility we hold the view that the Brazilian method gives a more uniform rate of cure because it is more uniformly applied by all seringueiros and does not lead to so many differences and causes of variation as in unstandardised preparation on estates. Further there is the possibility that it levels up, in a still unknown way, the effect of maturation or the amount of accelerators in the rubber.

The view that this uniformity is caused by the fact that one ball is built up from latex of several days and so constitutes an average over a certain period, can certainly not serve as an explanation. Though a certain amount of „averaging up” will result, this averaging would only explain

uniformity in the whole of the product from Brazil if latex not only from different days, but also and above all from different estrada's was coagulated in one ball. Plantation-rubber, obtained from one field or area, may be very uniform, when prepared after standard methods (see § 53, 66, 67, 132 and 154); the largest variability in plantation-rubber is not found in the product of one origin (for instance one estate), especially not when standard methods are adhered to, but between the product of different estates or districts, and is caused by the still unknown differences in composition of the latex (see Chapter II) which, with present methods of preparation on estates, retain their full influence in the rubber.

If therefore Brazilian balls, which each represent the product from one relatively small group of trees, are indeed as a whole more uniform in rate of cure than plantation-rubber as a whole, there must be a factor in the Brazilian method (be it in the trees, or in the method of preparation) which levels up variation caused by differences in the latex.

The *tensile strength* of Brazilian rubber has often been compared with that of plantation-samples; the conclusion generally was that plantation-rubber may equal or even surpass Brazilian rubber in this respect, though samples of inferior strength also occur.

Amongst the many data, scattered through the literature, we may mention the comparative tests by CL. BEADLE and H. P. STEVENS (I.R.J. 46 (1913), 111 and 161); further the large series of comparative tests published by S. MORGAN (Prep. Pl. Rubber, page 206—210), in which plantation smoked sheet nearly always showed better properties than Fine Hard Para.

About other properties of Brazilian rubber data are scarce. Differences in plasticity, viscosity, adhesiveness in solution, and perhaps in other vulcanising properties than the above, seem to exist, but have never been defined and followed up in a systematic way.

To allow a strict comparison with the figures given in this book, we may summarise the result of our tests on a few samples of Brazilian ball-rubber (Hard Fine) as follows:

Tensile strength	Standard time of cure	Slope	Viscosity
1.45	100	35—39	33

The tensile strength of these few samples was therefore better than the average of first quality plantation-rubber; the rate of cure is the same as for smoked sheet, whilst the slope was somewhat variable, and the viscosity the same as the average for crepe and smoked sheet.

§ 187. Brazilian method on estates.

Preparing the rubber after the Brazilian method has, of course, a great attraction and has repeatedly been tried in the East; but, as far as published results go, these were only trials on a small scale, executed by the investigators themselves. This, of course, may lead to balls of somewhat different composition from those prepared in Brazil or in the East by the tappers as part of their routine.

W. R. TROMP DE HAAS (Teysm. 13 (1902), 258) mentions experiments in coagulation after the Brazilian method in the Cultural Gardens at Buitenzorg. The rubber was judged very favourably in Europe, but details about its composition and properties are not given. Early experiments in Java are described by H. C. DINET (Teysm. 14 (1903), 339; *ibid.* 15 (1904), 237), in which the rubber was prepared in „balls or pelles” of 6 K.G. weight.

Experiments on a larger scale were conducted by R. DERRY in Singapore (Agric. Bull. Str. F. M. S. 9 (1910), 277 and 437; *ibid.* 10 (1911), 328; I. R. J. 42 (1911), 375). When freshly prepared there was a gradual exudation of water from the balls, so that part of the serum was removed in this way. The balls contained 17—25 % of water, which however sometimes during the voyage diminished to 13 and 9 %. The percentages of resin (3.4—5 %), protein (3.4—5.3) and ash (0.4—1.1) found in different tests, were mostly higher than in ordinary plantation-rubber. The viscosity was decidedly lower than for Fine Hard Para or ordinary plantation-rubber; but the adhesiveness was nearly the same as in Fine Hard Para, and the properties after vulcanisation were judged by several manufacturers to be quite equal (see for instance I. R. J. 42 (1911), 375).

For the analysis of a further large sample, prepared from latex of a single tree, see Bull. Imp. Inst. 10 (1912), 25, and Gard. Bull. I (1912), 151. The dry rubber contained 4.8 % resin, 3.1 % protein and 0.7 % ash, and in the acetone-extract 2.7 % quebrachite was found.

As a result of these experiments a process was developed by R. DERRY for coagulating latex in smoke on a revolving band (see Agric. Bull. Str. F. M. S. 10 (1911), 332, and Gard. Bull. I (1912), 81) which however found no application in practice.

G. A. VERNET (Bull. I. Ch. 14 (1911), 816; also C. Gp. 1912, page 5854) describes some difficulties in preparing balls on an experimental scale, namely that the latex does not adhere well to the ball, and that the fresh balls show a large deformation because the coagulum was weak and much serum presses out. His product was nevertheless judged by a manufacturer as equal to, and a second time slightly inferior to Fine Para.

S. MORGAN (Prep. Pl. Rubber, page 204) prepared two balls after the Brazilian method, but carried the heating so far that the moisture-content of the balls was much lower than in Fine Hard Para (one sample was dry on arrival in London, the other contained only 3% of moisture). These samples showed a higher resiliency, resistance to stretching and recovery than samples of Fine Hard Para tested at the same time; in one case the recovery after the Admiralty test was lower. These results, however, because of the low moisture-content of the samples, allow of no strict conclusions.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 493; also I. R. J. 51 (1916), 751, 791 and 829) made comparative experiments; he prepared two balls from latex of 15 and 5 year old trees, and smoked sheet from the same latices. One ball was prepared in the whole on one day, the other on four different days in the course of a month. The evaporation was evidently carried farther than in the experiments to be described below, as only a little bright brown serum came away from the mass during the first few days following its preparation. The balls were creped when 9 months old and found to contain 9 resp. 11 % of moisture. The vulcanisation tests gave the following results:

	Tensile strength	Rate of cure	Type
Smoked sheet from young trees	2264 lbs	1 ³ / ₄ hours	38
Ball from young trees	2411 "	2 ¹ / ₂ "	40
Smoked sheet from older trees	2192 lbs	2 ¹ / ₂ hours	36
Ball from older trees	2137 "	2 ¹ / ₂ "	38

The figures for tensile strength are regarded as of the same order; the ball in one case cures slower, in the other in the same time as smoked sheet, whilst the type (slope) in both cases is higher (worse).

The results for tensile strength and slope are similar to those from our experiments; but the large rate of cure of the Java-balls is not reached, either because the balls were brought immediately to a lower water-content, so that maturation could not proceed, or because the smoke (from rubber wood with atap palm nuts) had a stronger disinfectant action, which is the explanation given by WHITBY himself.

It was further found that the inner portions of the ball (moisture-content 13.1 %) had the same properties as the outer (4.5 % moisture) and especially showed no superior tensile strength, which some suppose would be caused either by the pressure exercised on the inner portions, or by oxydation of the outer layers.

Two balls, prepared in experiments by L. E. CAMPBELL in Ceylon (Bull. Ceyl. No. 27 (1916), page 21; Bull. Imp. Inst. 14 (1916), 537) do not give results directly comparable with ours, as they lost only less than 2.5 % on washing; they cured slower than the control unsmoked sheet, but quicker than ordinary smoked sheet; the tensile strength was somewhat inferior.

In Java, the rubber of the estate Sidoredjo near Semarang has since 1914 been prepared after the Brazilian method, and rather extensive experiments have been made on several other estates. The arrangement generally is as follows.

Every tapper makes his own ball, coagulating every day the latex he has collected; preparation takes him from $\frac{3}{4}$ to 1 hour. Special smoke-furnaces are used; on the estate in question these are all placed in one smoke-shed near the factory, but of course on large estates smoke-sheds might be erected in a number of suitable places, as supervision is easier than in the ordinary process of preparation. Large lumps are removed by sieving, small clots (curdling) do not injure the quality and need not be removed.

The balls are generally made up to a weight of appr. 10 K.G., which, depending upon the daily amount of latex, takes a tapper 7 to 14 days. The balls are then brought to the central store-house, weighed, kept for several months to shrink and dry, and weighed again. Coolies are paid by weight of rubber; but as the moisture-content of the fresh

balls may vary considerably, they receive the bulk of their payment on delivering the balls, and the rest as a premium, after some months, when the balls have been weighed again. One oven for every 3 tappers is found to be sufficient, as the tappers do not all arrive at the same time, and can use the ovens in succession.

The chief advantage of this method of preparation is that it saves the capital outlay for factory and machinery, and this may be important for instance for estates with a small plot of older trees, as the decision as to which kind of factory to erect may then be postponed till the larger young areas come into tapping. Though the balls are, to outward appearance, perhaps not equal to Fine Hard Para, prices have been very satisfactory.

The process is also being tried with small native holders, for whom perhaps it might be a marked improvement upon the present careless and unstandardised methods (use of alum, greatly diluted latex, careless drying in the sun etc.).

Large estates are not very inclined to follow this method of preparation, as there is additional work for the tappers, and a regular and strict control of tapping and production is not so easily arranged, because the exact dry weight of rubber only becomes known long afterwards.

In experiments on the production of individual trees over long periods this method of preparation has certain advantages, as it is easier to control, weigh, and keep separate a limited number of balls (one for each tree) than hundreds of small pieces of crepe.

See for instance P. J. S. CRAMER, Arch. 3 (1919), A 49.

§ 188. Details of preparation.

Though the preparation of balls in Brazil has often been described, details are scarce about some of the points which would interest the chemist most and might explain the process of coagulation and the properties of the rubber.

We give here some details that we have gathered in our experiments, without, of course, pretending that the same will hold good for preparation in Brazil.

The smoke was produced from some ordinary kind of wood (Hevea, coffee etc.); the temperature near the opening of the smoke-funnel was some 150—170° C, and near the surface of the balls perhaps 70—100°; the latex and fresh coagulum were never found hotter than 50°.

V. CAYLA (J. d'A. T. 13 (1913), 233) in Brazil found appr. 80° in the smoke near the balls, but the coagulating latex did not reach this temperature.

Coagulation with trained tappers does not meet with any difficulty; the latex, poured on the balls in small portions, very soon thickens. It takes on a dirty brownish white colour, which only gradually darkens. Often, when the coagulation of one day is finished, the newly formed layer does not adhere firmly all over to the ball; it is then pressed by hand, and often again in the afternoon, as serum not only sweats out on the outside, but may also collect in a pocket between the new and old layer, from which it is then removed by pressing.

On the next day the layer, light brown coloured, is firm enough to coagulate new latex on.

After coagulation, during the night, and during pressing a considerable amount of serum drips out; we collected from coagulum obtained from an „undiluted” latex with 22 % rubber, dripping serum to an amount $\frac{1}{3}$ to $\frac{3}{5}$ of the volume of latex, or $\frac{1}{2}$ to $\frac{4}{5}$ of the „original” serum. In some experiments the dripped out serum was found to contain 4—5 % dry substance and 0.8—1.0 % ash, so that it is somewhat more concentrated than the original serum. The whole of dripped out serum therefore certainly carries more than one half of the soluble serum-substances. The common belief that the Brazilian method keeps all the serum-substances in the rubber certainly does not hold good for the balls prepared on estates in Java, nor, as we saw in § 186, for the Brazilian balls.

When freshly prepared the balls have a light greyish brown colour, which on keeping gradually changes into dark brown and nearly black.

The actual dripping out of serum soon ceases, but a loss in weight by evaporation goes on, though with a diminishing rate, over months and years. Fresh balls may show a loss on washing of 30—40%, but after a few weeks this loss is only 20% or less, and three months after preparation the loss on washing is only 10—15%, decreasing further to some 10%. In old not too small balls the average is seldom below 8%, though of course the outer layers may contain less moisture.

The coagulum gradually hardens; in young balls it is somewhat weak, and these are classed not higher than the „medium” Brazilian grades. On keeping for one or two years the balls harden, and gradually come very near to the consistency of Fine Hard Para. As in the Brazilian balls, the interior, where oxydation is not possible, remains white; separate pockets of water, or free water dripping from the cut, are however seldom or never found.

§ 189. Composition and properties of rubber.

Composition.

Crepe, prepared from a ball from Sidoredjo estate showed the following composition:

Loss on washing in the ball	8—20 %
Moisture in air-dry crepe	1.5 %
Ash „ „ „	0.6 %
Acetone-extract of „	2.3 %

The moisture-content of this crepe is therefore somewhat higher than in ordinary crepe; the ash is higher than in ordinary crepe or sheet, and also somewhat higher than is generally found in Brazilian ball-rubber (see § 186). The acetone-extract shows a rather lower figure.

It may be remarked that, though the washing and crepeing of the balls does not meet with any difficulty, the rubber is rather more stubborn than ordinary plantation-rubber and sticks somewhat less easily together to form a coherent crepe, so that in this respect it takes an intermediary position to rubber containing all serum-substances (see § 193).

A further interesting point is that the balls in the wet season show a certain hygroscopicity and, though smoked

for some time on the outside after finishing, may get covered with a slight growth of moulds.

Properties after vulcanisation.

The balls, prepared on estates as described above, show a decided increase in rate of cure on keeping. Though of course the rate of the increase may differ from case to case, the following figures may be regarded as typical:

Crepe from latex diluted to 15 % and rolled next day	100 min.
Ball from same latex, undiluted; washed and creped a few days after preparation.	95 "
Same, washed and creped 1 month after preparation	80 "
Same, washed and creped 3 months after preparation	70 "
Same, washed and creped 6 months after preparation	65 "
Same, washed and creped 12 months after preparation	60 "
Same, washed and creped 24 months after preparation	50 "

In the first months therefore a rather rapid increase in rate of cure, which continues more slowly in the second year, till a really quick curing rubber, showing the rate of cure of fully matured rubber, is obtained.

Though proof is still lacking, it may be assumed that this increase in rate of cure is caused by a slow maturing process in the still wet ball, from which it would follow that the smoke, as used in these preparations, does not fully inhibit maturation, but perhaps slows it down.

The tensile strength was generally found between 1.36 and 1.42, that is the same as of crepe or smoked sheet; the number of strictly comparable samples, prepared from the same latex, is too small to allow of any conclusion as to an eventual small difference.

The slope lies between 38 and 40, and is therefore higher (less) than in ordinary plantation-rubber.

The viscosity is always low, generally between 15 and 30, mostly 20 to 25; it is the same in fresh as in old balls and does not increase at the same time as the rate of cure, so that the eventual maturation has not the same effect on viscosity as rapid maturation in fresh coagulum.

To judge of uniformity, especially in the product of different estates, our data are still too scarce. A strict comparison is, of course, only possible with balls of one year or older, to exclude the differences caused by maturation. It should further be remembered that a variation over 10 to 15 minutes, as we found it, is smaller than the ordinary variations in crepe or smoked sheet (see § 132 and 154); but calculated as percentage of time of cure, which affords a stricter comparison, the variations in balls of different origin (so far as can be judged from the relatively small number of samples) are not so much smaller than in the ordinary plantation-product.

It may be mentioned that the rate of cure of unwashed slices of balls, tested after air-drying, is nearly the same as that of the crepe obtained from it. We however found the tensile strength of unwashed balls sometimes to be low, perhaps owing to small particles of dirt or non-rubber substances; we therefore generally test this rubber only after thorough washing and crepeing with luke-warm water.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 498; also I. R. J. 51 (1916), 793) did not find a difference in tensile strength, rate of cure or slope to be caused by crepeing, against pieces of a ball simply dried in a desiccator.

We have also tested outer and inner layers of one ball, and found the differences small. The outer layer was once found to cure somewhat quicker and show a somewhat higher tensile strength than the inner portions (both washed and creped), and we could find no indications that the quality, or at least the properties after vulcanisation, of the inner layers are increased by the pressure exercised on them by the outer parts of the ball, or that the outer parts deteriorate somewhat by oxydation.

This factor was supposed to be important for Brazilian balls by many authors; see for instance. V. CAYLA, J. d'A. T. 13 (1913), 233; C. Gp. 1913, page 7775.

G. S. WHITBY (J. S. Ch. I. 35 (1916), 498; also I. R. J. 51 (1916), 792) found tensile strength, slope and rate of cure to be practically the same for inner and outer layers of his experimentally prepared balls. An eventual difference in structure or hardness of non-vulcanised coagulum is of course another question.

It is interesting to add a few figures for balls obtained from the latex of one tree over long periods, for instance a year. We tested a large number of such balls, and found the rate of cure between 75 and 95 minutes, mostly 85—90 minutes. In the first place it is evident that the rate of cure is slower than in ordinary balls. This may be explained by the lower moisture-content of these balls, built up of very thin layers resulting from the small daily quantities of latex from one tree, so that less moisture is retained than in ordinary balls: the loss on washing of fresh balls is only 10—15 % and diminishes only by a few percent in the course of a year.

Maturation takes place, but to a less degree than in ordinary balls; the time of cure may for instance decrease from 85 to 70 minutes.

The figures for individual trees, once the increase in rate of cure caused by maturation is finished, do not seem to vary as much as when crepe is prepared (see § 22). A strict comparison between ball and crepe has only been made for a limited number of trees, and it remains to be seen whether in the preparation of ball-rubber the differences in composition of the latex are levelled up to a certain extent, more so than in preparing crepe.

The tensile strength in balls from individual trees shows some variation, but it could not yet be stated with certainty whether this is a constant difference between the trees. The slope is generally found between 38 and 40 and shows little variation, whilst the viscosity shows the ordinary low values for ball-rubber. A direct relation of viscosity in (creped) ball-rubber and in crepe from the same latex could not yet be found.

§ 190. Discussion and explanation of properties.

Many authors have offered explanations and hypotheses on the properties and the supposed superiority of Brazilian

balls; but generally the experimental proof is lacking, whilst on certain points the supposed difference between Brazilian balls and plantation-rubber was more suggested than expressed accurately in figures.

For discussion of factors that may play a role in the Brazilian method see for instance R. H. BIFFEN, *Ann. Bot.* 12 (1898), 166; V. CAYLA, *J. d' A. T.* 13 (1913), 231, *C. Gp.* 1913, page 7775; G. VERNET, *Bull. I. Ch.* 14 (1911), 818; also *C. Gp.* 1912, page 5857; and G. S. WHITBY, „The prime technical plantation problems of the next decade” (*Batavia Rubber Congress, Weltevreden 1914*), page 17.

Some of these hypotheses have been tested subsequently. That the pressure exercised on the inner layers by the shrinking of the ball does not lead to any amelioration of the properties after vulcanisation, has already been discussed in § 189. It has been shown also that the oxydation of the outer layers, causing their nearly black colour, does not cause a deterioration of the properties of the rubber after vulcanisation.

See G. S. WHITBY, *J. S. Ch. I.* 35 (1916), 497; also *I. R. J.* 51 (1916), 792.

The supposition that the uniformity of Brazilian balls is caused by their being built up from latex of different days was found an insufficient explanation (see § 186).

We will now discuss some further factors, which may be of importance. The following points would thereby have to be cleared up:

Brazilian balls have approximately the same composition, the same tensile strength, rate of cure and viscosity, and perhaps a somewhat larger slope than smoked sheet.

Balls prepared in Java have the same tensile strength, a much larger and gradually increasing rate of cure, a larger slope and a lower viscosity than crepe from the same latex.

The most important causal factors are:

1. Age of the trees.

The trees in Brazil are on the average much older than on plantations, and this has often been supposed to cause a superior tensile strength and a better rubber. We may

now assume that the tensile strength of Brazilian ball-rubber is not per se better than that of plantation-rubber, and this agrees with what we found in § 24, that the tensile strength of trees of 8 years and older does not show any difference in relation to age.

Older trees were found (see § 24) to give a somewhat slower curing rubber with a higher viscosity. Whether this is also the case with the trees in Brazil remains to be tested, but probably this factor will have to be taken into account, and perhaps it may explain, at least in part, the slower cure and higher viscosity of Brazilian balls compared with those from Java.

2. Content of serum-substances.

The supposition that the balls contain all the serum-substances was shown in § 186 and 188 to be false, and a greater rate of cure from this source need not be expected. The balls, and more so the crepe obtained from them after washing, are nearer in their composition to smoked sheet than to Kerbosch-rubber (§ 193) or dried up films of latex (§ 102).

3. The action of heat.

Coagulation of latex by heat gives a quick curing rubber with a low viscosity and large ash-content (compare § 100)¹⁾. Such coagulation takes place at 70° C, but at lower temperatures also when the latex contains more acid. The coagulating latex on the balls we tested was never hotter than 50° C, but may have absorbed acid or other coagulating substances from the smoke, so that a coagulating effect of the temperature of 50° is not excluded. Nevertheless, a strict coagulation by heat probably does not take place, as the latex on the balls does not clot or form a visible coagulum, but thickens as a whole. The accelerating effect of coagulating by heat is not yet explained (see § 100); but it is doubtful whether this factor enters into the preparation of balls, as a fresh ball does not cure much quicker than ordinary crepe

¹⁾ In the table on page 218 the first line should read „Control coagulated by acetic acid”, and the second line „Coagulated by heating the latex”. See *Corrigenda*.

(see § 189). Whether the low viscosity of ball-rubber may be explained by the action of the heat remains to be seen; it is already found in the fresh balls, and also in Kerbosch-rubber, whilst films of latex dried up at ordinary temperature (see § 102) do not show a lower viscosity. Only strictly comparative experiments can decide which factors are responsible.

4. *Evaporation.*

Evaporation by the stream of hot smoke certainly plays a role; when studying coagulation on the balls as it proceeds, a thickening of the latex by evaporation would seem the first stage.

Probably the factor „evaporation” eo ipso, the simple loss of water, has no effect on the properties of the rubber

5. *The smoke.*

A beneficent effect of smoking has been claimed by many authors; and perhaps it has an effect on the firmness and hardness of the coagulum, which however has never been expressed in figures. Further, it certainly prevents or hinders mouldiness and spotting by micro-organisms. It has been shown (compare § 146) that smoke retards vulcanisation somewhat, but does not alter the properties after vulcanisation.

Probably the smoke enters as an explaining factor in the preparation of balls: the rate of cure will be retarded by some of its constituents (phenolic bodies and so on) and it may inhibit or retard maturation. No figures are available as to whether the balls in Brazil show a maturation (increase in rate of cure) during the first months after preparation, as is the case with the balls made in Java, where the smoke does not seem to inhibit, but only to slow down maturation. It may of course be that the smoke used in Brazil has a stronger inhibiting action on maturation than the rather thin smoke used in Java, but nothing is known about it. The phenolic bodies in the smoke probably help to give the ball-rubber its nearly black colour, where oxydation is possible; whilst the acids contained in the smoke may help coagulation.

6. *Moisture-content.*

The fresh balls contain a large amount of water, which on keeping diminishes to some 15 or 10%, so that enough remains for maturing processes to take place. Whether these are found in Brazilian balls is unknown; balls made in Java showed a pronounced increase in rate of cure on keeping (see § 189).

From the foregoing it will be clear that the great rate of cure of Java balls is explained for the greater part by maturing and perhaps by some other factors influencing the initial rate of cure; the explanation of the other properties, and the actual influence of the different factors mentioned above, must wait till sufficient experiments have been made.

The smaller rate of cure and higher viscosity of balls from Brazil must also remain unexplained, as long as no data from experiments in Brazil are available. It might however seem probable that a somewhat slow rate of cure is caused in the fresh balls by the age of the trees and the smoke-constituents, which then, by maturing, increases to the value found for smoked sheet.

The interesting fact that the balls prepared on estates in Java cure so much quicker than the balls from Brazil was mentioned in § 186 and indicates that there is at least one factor in this process which, being different in Java and in Brazil, may cause large variations in rate of cure.

CHAPTER XV.

SPECIAL METHODS OF PREPARATION.

§ 191: Preparation of pressed and blockrubber.

In the first years of the plantation industry much was expected of the preparation of blockrubber, the crepe being vacuum-dried and pressed into blocks while still hot. The rapid preparation, the compact form, and especially the minimum surface exposed to air, moisture and oxydation, were regarded as so many advantages over the ordinary form of rubber.

Manufacturers recommended this form of rubber, and its use has again been advocated from time to time up till the present.

See for instance Ceyl. R. E. 1906, page 129, 76 and 77; Agric. Bull. Str. F. M. S. 6 (1907), 291; further G. LAMY-TORRILHON in J. d'A. T. 8 (1908), 35 and 9 (1909), 259.

A recent plea for blockrubber was made by S. MORGAN (Mal. T. & R. J. 7 (1918), 1024) who stated that blockrubber can be kept for a very long time without changing.

This pressing of the rubber into blocks of about 5 c M. thickness, from which so much was and is expected, was not encouraged by the market; and to day, so far as is known, there are only a few estates that work their product in this form. Even the urgency of economising in shipping space during the war did not stimulate the preparation of blockrubber; it only led to more compact packing and to pressing the sheet or crepe into the chests.

It seems that the fear of dirt or other impurities in the interior of the blocks is so paramount that this form of rubber cannot find favour; thin crepe and sheets, which can be separated and inspected at will, do not arouse the

suspicion of the buyer or broker, though a lot of dirt, chips of wood etc. may get between the folds during transport, and may necessitate considerable expense in picking and rewashing. To one who is intimately acquainted with the plantation industry there is not the least doubt that estates would produce blocks just as pure and unadulterated as their crepe or sheet is now-a-days; and why the rubber, which leaves the estates in a clean form, should be left to get mixed with dust and dirt, instead of being pressed while it is still pure, is not easy to understand.

Remarks on the preparation of blocks and the occurrence of air-bubbles therein see S. MORGAN, Prep. Pl. Rubber, page 100 and 165.

Blocking the rubber, as a mere mechanical process, does not change its inner properties. The idea that pressing makes the rubber stronger is wrong, at least as far as the vulcanising properties go; of course the raw product may be somewhat changed by pressing, and perhaps also alter in velocity of dissolving and such properties; but the reconstruction during vulcanisation wholly effaces such differences (compare § 105 and 106).

In so far as blocking is accompanied by vacuum drying and heating, the changes treated in § 125 may occur.

Blocking dry crepe was found to be without influence on the rate of cure and tensile strength of the rubber in experiments by L. E. CAMPBELL (Bull. Ceyl. No. 27 (1916), 5, 8 and 27; Bull. Imp. Inst. 14 (1916), 554 and 565). The amount of pressure exercised in blocking was also found to be without influence. Pressing wet crepe into blocks either with or without disinfectants such as creosote gave a rapid curing rubber, as was to be expected.

B. J. EATON, J. GRANTHAM and F. W. F. DAY (Bull. F. M. S. No. 27 (1918), 259) found that blocking worm-rubber after hot air drying gives a rubber of somewhat smaller rate of cure than usual, whilst the tensile strength may also be somewhat inferior. They recommend maturing the coagulum first and then blocking it (see the next paragraph).

Blocking the rubber while still wet, after adding a disinfectant to the latex to avoid putrefaction, was already recommended in the early days of plantation-rubber, and

regarded as one of the best methods of preparation. It leads to rapid curing rubber, maturation taking place. This form is closely related to the preparation of slabrubber (see next paragraph) and, apparently for the same reasons, did not find favour.

See J. C. WILLIS and M. K. BAMBER, *Circ. R.B.G.* 4 (1907), 1 and the above mentioned experiments by L. E. CAMPBELL.

§ 192. Preparation of slabrubber.

Slabrubber, in the strict sense of the word, is rubber produced in the form of thick cakes, in contrast to sheets and crepe. Since these thick cakes always dry slowly and maturation therefore takes place, the term slabrubber is often used for matured rubber in general, and even the term „slab-crepe” (at first perhaps striking one as a contradiction in terminis, but meant as crepe from slab) is used for crepe from matured rubber.

We have fully discussed the maturation-processes and the properties of matured rubber in § 108. For the question to be treated here, viz. the preparation of matured rubber on a large scale and as a marketable product, the following points may be recalled to memory:

1) matured rubber vulcanises very quickly, shows an accordingly higher tensile strength and viscosity, and a small (good) slope. Its vulcanising properties are therefore superior; but what the value of this superiority is for the manufacturer, and what amount it will represent in the market price, is not yet sufficiently known.

2) the maturation is accompanied by a loss in weight, which may amount to $2-2\frac{1}{2}\%$, but which in preparation on a large scale will probably be about $1-1\frac{1}{2}\%$ (see § 108, page 243).

As far as preparation goes, spontaneous coagulation (preferably in the absence of air, see § 95) gives the best results (quickest rate of cure); the saving in acetic acid in this procedure is approximately neutralised by the loss in weight (ca 1%).

The putrid smell of maturing rubber, which persistently sticks to the clothes and the skin, and is especially bothersome the more it is diluted, makes maturation little beloved in planting circles, whilst manufacturers also seem to object to it: the story that workmen having handled a lot of this rubber were turned out of a streetcar as unfit for society is well known. The smell can be overcome by using suitable disinfectants; this, of course, adds to the costs of preparation.

Patents for the use of β -naphthol for this purpose see I.R.J. 56 (1918), 122; I. R. W. 58 (1918), 655; J. S. Ch. I. 37 (1918), 313 A.

We now come to the further question: in what form should matured rubber be delivered?

The simplest form, of course, are the slabs of 1 to $1\frac{1}{2}$ inch thickness which are now being experimented with on a large scale, and attracting the special attention of planters, because they not only do away with the greater part of the milling (the coagulum being passed only once or twice through widely opened rolls), but also abolish the remarks and complaints on faults in the exterior appearance of the rubber — the great bogey for planters, who know very well that the real value of their product is not in the least impaired by these faults.

Delivering the rubber in thicker or thinner cakes or slabs, simple as the method of preparation is, has however the drawback that the product contains a rather large amount of moisture (some 12 to 20 %), which has to be taken into account when fixing the price. Not only is the moisture-content of the interior of the slabs higher than of the dried up outer layers, but it may vary several percent from sample to sample, and from lot to lot. Sampling and determining a reliable average figure requires adequate care, and this uncertainty in the rebate for moisture brings a factor into the marketing of this product, which is so luckily absent with ordinary crepe or sheet.

Of course, the matured slabs may be creped and dried. But apart from the fact that the crepe thus obtained is dull coloured and often streaky, and does not fit in with what is now-a-days regarded as standard, the crepeing of the old, hard coagulum takes much more time and engine-power

than the milling of fresh coagulum, whilst the resulting crepe dries very slowly and requires a large drying space. If this method had to be adopted on estates, the price of the product would not only have to make up for the loss in weight (see above) but also for the more troublesome and costly preparation.

To overcome the slow drying of the crepe, it has been proposed to cut the matured coagulum into pieces by some kind of worm-cutter, to vacuum-dry these, and to press them into blocks.

See B. J. EATON, *Agric. Bull. F. M. S.* 5 (1917), 183 and 6 (1917), 150; further *Bull. F. M. S. No. 27* (1918), 259.

This method would solve the above difficulties; but it involves further expense, and all depends upon the price manufacturers are willing to pay for the natural accelerator, incorporated in the raw rubber, instead of artificial accelerators.

The preparation of matured rubber is still in the stage of large scale experiments. If a regular market for this product, preferably in its simplest form of thick slabs, could be established, this would in our eyes be a distinct advantage as smoked sheet or crepe might then be replaced by slabs in circumstances where this would suit estates better. The opinion of manufacturers, however, seems not yet settled on this subject and, of course, creating a market for this form of rubber has its special difficulties.

§ 193. The Kerbosch-process.

As we already mentioned in § 98, a very large number of processes, patented and unpatented, have been described to replace the ordinary estate-procedure; mostly they were meant as a substitute or even an improvement on the Brazilian method of smoking balls. Some of the contrivances invented in the course of years are very ingenious — though mostly impractical and not fit for use on estates; none of them has found favour, and even trials in such directions are getting more and more scarce.

We will not enumerate and describe these processes, as we do not possess special experimental data on their effect;

only one of these procedures, which is moreover of a certain theoretical interest, was studied more extensively and will be treated here.

This process, patented by Dr. M. KERBOSCH, consists in total evaporation of the latex by a strong current of hot air and runs as follows.

The undiluted latex is poured on the inner bottom of a large drum, lying in a horizontal position, which is open at both ends and is about 2 M. in diameter and 1.8 M. long. This drum is supported by disks and slowly revolved by a belt, raising with it a thin layer of the latex on its inner surface. Through holes in a pipe which runs lengthwise down the centre of the drum a strong current of hot air is blown, which is quickly spread over the entire inner surface by paddles revolving rapidly in a direction opposite to that of the drum, so that the latex adhering to the drum quickly evaporates and solidifies before a half revolution of the drum is completed. The thin film, when moving downwards during the remainder of the revolution, dries up to a great extent, till it is covered by fresh latex when passing the lowest point and so covered during further revolutions by layer on layer of rubber. The temperature of the air, where it is blown in, was 60—70° C in the experiments we attended; the inner surface of the drum was found to be 50—65°, while the iron of the drum itself reached 45°. The latex below in the drum must not become too warm (not above 40°), since curdling or clotting may then occur, so that the film becomes irregular and full of lumps; by adding fresh cool latex one may attempt to regulate the temperature of the latex, but this requires a great deal of care, and the thorough regulation and control of the procedure is not so simple and demands continuous attention — at least with the apparatus experimented with some time ago on an estate on Java.

This constant supervision, added to the rather costly installation (one drum works only about 50 liters of latex per hour), are disadvantages against which must be placed the saving in ordinary costs of preparation, and the not unimportant increase in weight of some 10 % by incorporating all of the serum-substances into the rubber. It remains

further to be seen whether this quicker curing rubber, with its higher content of serum-constituents, has such special properties that it will fetch a higher price on the market.

Kerbosch-rubber is a rubber obtained by true evaporation of the latex and contains all serum-constituents. Since the films thus obtained are somewhat sticky and greasy, and adhere to each other, it has been attempted to wash them with water so as to make them easier to handle; in so doing a small part of the serum-constituents are, of course, soaked out.

In the first experiments thick films of 3—4 mM were made and then pressed together into slabs of about 1 cm thickness. These were brownish black in colour, because they were dried in a smoke room. They contained a great deal of moisture, the loss on washing was 6—8 %, and between the layers, which easily separated, drops of moisture might be found, especially when the samples were fresh.

On prolonged keeping these films became drier and less hygroscopic. Whether or not maturation had taken place is still unknown; but the possibility remains, since the time of cure was about 60 minutes, or somewhat less than that of later samples (80 minutes), but about as large as that for crepe coagulated by heating the latex (which crepe, of course, does not contain all the serum-constituents, see § 100) ¹⁾. The viscosity was 15—25, therefore the ordinary low value for rubber obtained by heating the latex. The slope was 38—40, the tensile strength normal.

The chemical composition was as follows:

Moisture-content	3—9 %
Ash	1½—2 %
Acetone-extract	3—4 %
Nitrogen	0.75—0.85 %

¹⁾ In the table on page 218 the first line should read „Control, coagulated by acetic acid”, and the second line „Coagulated by heating the latex”; see *Corrigenda*.

Compared with the composition of ordinary crepe or sheet the moisture- and ash-content are considerably higher, the acetone-extract is somewhat higher, and the nitrogen-content is decidedly higher.

Samples of older experiments, tested at Delft (see Comm. Delft II, page 41—66) gave the following figures:

Moisture-content . . .	3.6 —3.9 %
Same after washing and air-drying . . .	1.8 —2.6 %
Acetone-extract some- what more than. . .	3 %
Nitrogen.	0.75—0.85 %
Ash	1.6 —1.8 %
Watery extract . . .	5.6 —6.6 %

Later experiments with a better apparatus produced thin films (of only 1—2 mM thickness) which already during preparation had become dry or almost so, and eventually were dried completely in vacuo. In part these films were quite transparent and light yellowish brown in colour, and in part an opaque white. The chemical composition was almost the same as above, the moisture-content 4—5 $\frac{1}{10}$. Maturation was in these cases practically excluded by the low moisture-content. The time of cure was found to be 70—80 minutes, the viscosity fluctuated rather widely but remained below 25. The slope for the later samples was 36—38, the tensile strength 1.31—1.35, therefore somewhat lower than in the ordinary estate product.

Taking all data together one can say that the rubber prepared according to the Kerbosch-process has the ordinary or a somewhat smaller tensile strength, a larger rate of cure, a normal or a somewhat greater slope, and a low viscosity.

A comparison of this method of preparation with the Brazilian method may be of interest.

The Kerbosch-rubber contains all serum-constituents and no foreign substances; the ball-rubber loses the greater

part of the serum-constituents by sweating, but contains smoke-constituents.

Although strictly comparable experiments, with portions of the same latex, have not yet been made, it may be concluded with sufficient certainty that the tensile strength in both processes is nearly the same and similar to that of ordinary plantation-rubber; that the slope in both processes is somewhat greater, and the viscosity considerably lower than with crepe or sheet.

The rate of cure is probably larger for Kerbosch-rubber (80minutes) than for freshly prepared ball-rubber (95—100min.), and on the one side the presence of all serum-constituents, which accelerate, on the other side the presence of smoke-constituents, which retard, are sufficient to explain this difference.

In the ball-rubber, however, maturation is slowly taking place, which reduces the time of cure gradually to about one half its former value (that is to about 50 minutes), while in Kerbosch-rubber no maturation takes place and the rate of cure remains constant.

Compared with crepe obtained by heating the latex, which does not contain all serum-constituents, Kerbosch-rubber has the same tensile strength, perhaps a somewhat greater slope, and an equally low viscosity, while the rate of cure appears to be somewhat smaller. The exact explanation is not yet to hand.

Although an exact insight into these differences can only be obtained by further experiments, from the foregoing it appears evident that the difference in content of serum-constituents in the above three types of rubber has no noticeable effect on the inner properties. The presence of all the serum-constituents in the Kerbosch-rubber makes itself most felt in the fact that the sheets are sticky, and also in the moisture-content which amounts to 4—5 % in dry transparent films, and which in air-dry crepe prepared from these films is still about 4 % (the loss on washing being only 0—1½ %).

The principal aim kept in view in working out this method was the manufacture of a rubber which in properties would resemble the Brazilian rubber as nearly as possible. So far as the inner properties are concerned this appears, according to the foregoing, to be nearly reached; the rate of cure was even somewhat greater in the samples of this type than in real Para-rubber, which vulcanises in about the same time as ordinary smoked sheet (see § 186). There is, however, a marked difference in composition, especially in the content of serum-substances. The inventor supposed that the rubber would be more durable and less susceptible to oxydation, if all serum-constituents were retained. Experiments as to the keeping qualities and the susceptibility to oxydation of rubber prepared by this method have not yet been concluded, and so on this point one still remains in the dark. Besides, the eventual advantages to the rubber manufacturer of the Brazilian method of preparation have never been defined and fixed in a scientific way, neither is it known whether the presence of the serum-constituents makes the rubber more valuable, be it in general or only for special purposes.

As long as no verdict is given in regard to these questions by the manufacturers or by scientific research work, final judgment as to the eventual superiority of these processes will have to be suspended.

§ 194. Electrical coagulation.

A great deal of interest was awakened by experiments in electrical coagulation, done on an estate in Java. The fact that the market is suspicious of everything that deviates from the normal, and further the somewhat deficient colour of the crepe thus obtained, have resulted in this type of rubber being no more prepared on a large scale. Further experiments are planned, and it may be of some importance to communicate the provisional data we collected on the process.

The method of coagulation and the first results have been published by S. CLIGNETT (Rubb. Rec. 1914, 377; C. Gp. 1915, page 8721).

Former experiments by COCKERILL in Ceylon are mentioned by J. PARKIN (Trop. Agric. 35 (1910), 8); patent description see Z. Koll. 7 (1910), 174.

In the first place it may be stated that, though the electrical current has been found to carry the rubber globules to the anode, the electrical coagulation as effected on a large scale is by no means simply explained by this phenomenon, and is probably of a more complicated nature. Electrolysis of serum-constituents, and of the electrolytes added to the latex, may play a role, and a further study of this process may perhaps bring to light many interesting points. The speculations on the character of electrical coagulation, found here and there in literature, are partly unproved, partly perhaps incorrect.

V. HENRI (C. R. 144 (1907), 432) found that the rubber globules of a preserved dialysed latex in an electrical field wander to the anode, so that after 4 or 5 hours the liquid in the neighbourhood of the cathode becomes clear, whilst the latex near the anode gets thicker; from which he concludes that latex is a negative emulsion. Natural undialysed latex has not yet been investigated on this point.

In our experiments on an estate in Java coagulation was brought about by an electric current from a small dynamo; the voltage was probably 110, the strength of the current could not be determined. As electrodes porous pots of Leclanché elements, filled with carbon, served on either side. To the undiluted latex, which contained about 30% rubber, 5 gms of sodium thiosulphate per liter were added; the influence of this chemical on the properties of crepe was discussed in § 49 and found to be small.

After turning on the current a coagulum quickly separated everywhere in the latex and on both poles; many times it formed a solid mass from pole to pole, and convection by the current could not be clearly observed. The coagulation was mostly effected in fractions, so that the product first obtained acquired the characteristics of a pre-coagulation (see § 176). Some figures may be quoted to illustrate the results of this method of preparation.

	Weight, % of the total	Tensile strength	Standard time of cure	Slope	Viscosity	Ash	Acetone- extract	Nitrogen
Control, acetic acid coagulation . .	100	1.32	120	37 $\frac{1}{2}$	25	0.32	2.8	0.52
Electrical coagu- lation as a whole.	100	1.34	> 80	36 $\frac{1}{2}$	27	0.44	2.8 ⁵	0.54
First clot from elec- trical coagulation.	21	1.41	> 65	37	58	0.95	4.1 ⁵	0.61
Second clot from electrical coagu- lation	21	1.52	< 80	37	47	0.43	2.6 ⁵	0.53
Third clot from electrical coagu- lation	55	1.43	> 80	36	22	0.45	2.4 ⁵	0.40
By heating the serum of electrical coagulation . .	3	1.44	40	53	27	0.63	2.6	0.17

The first clot was obtained after the current had been turned on for a quarter of an hour; the lumpy mass was then lifted out of the latex by hand, and as much of the latex as possible was pressed out. The great rate of cure and the high viscosity, as well as the chemical composition, correspond entirely with those of pre-coagulated latex (see § 176).

The second clot was collected after the current had been on for half an hour more; the third fraction coagulated without further electric stimulus during the night, and had the smell and the yellow slimy layer of spontaneously coagulated rubber. Both second and third clots had approximately normal composition, but vulcanised somewhat faster than was expected, and the viscosity of the third fraction was low. By heating or boiling the serum some rubber was still obtained, but this product, which vulcanised very quickly, was of very inferior properties, as is clearly seen from the high figure for slope (53).

Perhaps of more importance is the following experiment, in which samples prepared by acetic acid were used as controls.

	Tensile strength	Standard time of cure	Slope	Viscosity
<i>Acetic acid coagulation</i>				
from 15% latex, without hypo	1.41	110 min.	37 1/2	31 1/2
from 15% latex, with hypo	1.39	> 105 "	38	35
from undiluted latex with hypo	1.39	< 100 "	38	38
<i>Electrical coagulation</i>				
first clot.	1.41	70 "	36	46
second clot.	1.44	85 "	36	38
from the poles, burnt. .	1.10	135 "	36 1/2	23

The acetic acid samples give the ordinary differences in properties caused by dilution of latex and addition of thiosulphate, already discussed in § 64 and 49. The rather large rate of cure is to be ascribed to the fact that the crepe was rolled rather thick and dried slowly. The electrical coagulation gave a product which vulcanised more quickly, while the first clot especially has a very large rate of cure and a high viscosity; the second clot also vulcanises more quickly than the control.

That the coagulation must be adequately controlled may be seen from the last mentioned figures for a clump of coagulum on one of the porous pots which became hot, whereby the temperature of this piece of rubber rose to about 50° C and it became burnt to some degree. The tensile strength and viscosity are very poor, whilst the rubber vulcanises comparatively slowly.

As we said above, further experiments, which are necessary wholly to clear up this method of coagulation, are still wanting.

§ 195. Sundry methods of preparation.

In the course of years many different methods of preparation have been tried or used for a longer or shorter time, but as

only little data concerning their influence on the properties of the rubber have been collected, there is no reason to discuss them here.

Many of these methods are based on the effect of smoke or smoke-constituents, often in combination with heating the latex, as was described in § 98, 100 and 193.

Other processes principally aim at economising acetic acid; several of these have been treated in Chapter VI.

A number of proprietary coagulants have been proposed, but none of them has been able to replace the ordinary procedures.

On *coagulatex* (sulphuric acid with some sodium chloride) see B. J. EATON, Agric. Bul. 4 (1916), 355. It has the drawbacks of sulphuric acid, and is much more expensive.

A few words may be devoted to a process which is patented under the name of Standard Rubber Process, Iicken-Down Patents. It consists in spontaneous coagulation in the absence of air, with the addition of a small quantity of a special coagulant, the composition of which varied in the course of years. It mostly consisted of alcohol with some glycerine, coconut-oil or fusel oil.

Patent descriptions see J. S. Ch. I. 35 (1916), 854; I. R. J. 54 (1917), 826; I. R. W. 54 (1916), 628, and 58 (1918), 562; C. Gp. 1917, page 9193; *ibid.* 1920, page 10141.

The idea of the inventor was that the rubber is formed by the tree in the latex-vessels, so that latex must contain the substances from which the plant produces rubber. It was supposed that the enzymes or other agents producing the rubber could be preserved and kept active by adding a special coagulant, so that rubber could be further formed in the latex after tapping during this method of spontaneous coagulation. The substances from which rubber is formed by the tree were supposed to be of a terpene-like nature and volatile, so that they evaporate during the ordinary process of coagulation and drying. An increased yield of 5 to 15 % (probably partly rubber, partly proteins and other serum-constituents) was claimed by the patentees to have been obtained in many experiments, but could not be observed by other investigators who busied themselves with this process.

As the total of the solid constituents that remain in the serum after acetic acid coagulation only forms some 10 to 12 % of the rubber, an increase in weight of 10 or 15 % would, really, be somewhat unexpected.

Already years ago F. KAYE (I. R. J. 40 (1910), 903) drew attention to the possibility of volatile substances being lost during the drying of rubber (compare also § 241 on the „moisture“-content or loss on heating), but such substances have never been isolated nor their amount determined, and it seems very doubtful that Hevea latex should contain an appreciable amount of such substances, though perhaps in other latices, such as the Plumeria-latex investigated by KAYE, they may play a role.

As for the supposed increase in yield by the Icken-Down process, experiments in the Botanic Gardens, Singapore (see I. R. W. 58 (1918), 562) are mentioned, which gave an increase in weight of about 5 %, whilst a series of experiments on an estate showed approximately the same increase.

B. J. EATON (Bull. F. M. S. No. 27 (1918), 276) examined the point and found the claim to an increase in weight incorrect.

In two series of accurate experiments we once found, instead of an increase, a loss in weight of 1.3 % as compared with ordinary crepe-preparation, corresponding with the loss in rubber in the milky serum; the other series gave equal weights.

To harden the coagulum and to precipitate some rubber from the milky serum a second coagulant (a mixture of alcohol and petrol) is added the next morning, and the coagulum rolled a few hours later.

Since the colour of the crepe may be somewhat dull and greyish, as usual after spontaneous coagulation, the finished crepe is soaked for one night in a bisulphite solution, acidified by sulphuric acid. The colour is then very pale, and with special precautions a pale yellow, good looking sheet may also be produced.

The properties of the rubber were found to be in the main the same as after ordinary preparation, but the keeping qualities, which deserve special attention after the final acid bath, have not yet been determined.

Further discussion see B. J. EATON, Bull. F. M. S. No. 27 (1918), 271—275.

CHAPTER XVI.

§ 196. Some common but incorrect opinions on rubber-preparation.

In closing these chapters on the preparation and properties of plantation-rubber we cannot refrain from exposing, and if possible correcting, some very common and wide-spread opinions on the preparation of rubber, which have a certain fascinating probability and thereby present themselves over and over again, but are nevertheless quite incorrect.

Many of these opinions were expressed — be it without sound proof — by prominent men in the rubber-industry some ten or fifteen years ago, when relatively little was known concerning the preparation and inner properties of the plantation product; uttered in technical papers or at congresses and other occasions, they found acceptance, because in themselves they were plausible. But when closely investigated in experiments, it becomes clear that they cannot stand the test and criticism of the scientific worker.

1). Hevea latex does not cream; whenever the latex is allowed to stand, the rubber-content will remain the same in the upper layers as in the lower ones (at least as long as no coagulation or curdling takes place).

Latices from other botanical origin do cream, and amongst them some of those from the varieties that were planted in former years side by side with Hevea, such as *Manihot* (Ceara) and *Castilloa*. Hence the persistent idea that Hevea-latex also creams, which idea is further supported by the curdling or clotting in premature coagulation, though the particles then rising to the surface are coagulated rubber, and no longer rubber globules as they are found in latex.

In close connection with the above stands the fact that by centrifuging Hevea-latex rubber cannot be obtained, in contrast with Ceara- and Castilloa-latex, in which the rubber can be separated from the serum by mechanical means.

One still often hears it asserted that Hevea-latex creams, and that for instance in a mixing tank the rubber-content after some time is greater above than in the lower layers. This, however, must be based upon incorrect observations; well mixed latex keeps for hours the same rubber-content below as above, so long as no coagulation or curdling takes place. The cases in which the contrary was supposed to have been observed were probably due either to a beginning of separation or clotting, or to incomplete mixing of the heavier water with the lighter latex.

2). Rubber coagulated from undiluted latex is not of a better quality than that from diluted latex.

One often hears the opinion that the dilution of latex cannot possibly be beneficial to the quality of the rubber.

In so far as one means the dilution with dirty water, there is certainly a lot of truth in this opinion; but in § 64 we showed that dilution with clean water has no unfavourable effect, and in § 67 that thinning to a standard content greatly improves the uniformity.

It is only when diluting the latex excessively, perhaps to 2 % rubber-content and less, that the properties of the product begin to deteriorate somewhat. But the ordinary thinning to 15 or 10 %, which so much facilitates preparation, is in no way detrimental.

3). The use of sodium bisulphite and some other chemicals is not harmful, but favourable for the properties of the rubber.

Although bisulphite is now very generally in use, one still often meets with the opinion that it would be better for the rubber if no chemicals at all were used. To be sure this would be cheaper, and that is a weighty argument. But, for the rest, bisulphite has a

good effect in all respects: it improves the external appearance, it may improve the inner properties (though to a restricted degree), and it improves the uniformity (see § 48).

The fear of traces of chemicals, incorrect as it may be in the above meant cases, is, by the way, very comprehensible, as traces of other substances may cause a very marked deterioration. For instance traces of copper compounds (see § 169), or traces of alkali (§ 106).

In the case of bisulphite it may be pointed out that during preparation this substance changes to sodium sulphate. Now the ash of rubber contains both sodium salts and sulphates, and in an amount greater than the traces that are incorporated in the rubber from bisulphite added to the latex. As mentioned in § 48, the use of bisulphite in the latex can generally not be detected from an analysis of the ash of the rubber.

4). Rubber which is coagulated spontaneously, without using acetic acid, is not superior for this reason; acetic acid, added in the usual quantities, has no harmful effect on the rubber.

The supposition that coagulation with acid cannot be good for the rubber, and that a naturally coagulated product must be better, is exceedingly persistent.

In § 94—97 it was shown, and this is the best argument to prove the incorrectness of the above supposition, that in spontaneous coagulation acid is formed in a much greater quantity than one is accustomed to add in the form of acetic acid; while this acid is for the greater part lactic acid, which is not volatile, and so would be more likely to remain in the dry rubber than traces of the volatile acetic acid.

In agreement with this no superiority could be found in rubber from spontaneous coagulation (see § 94 and 95).

Traces of acid certainly decrease the viscosity of rubber-solutions markedly, but this, at least in the beginning, is only due to the change in the solving medium, and not to a deterioration of the rubber (see § 232 and 236). In how far traces of dilute acids are

injurious to raw rubber, is not yet sufficiently known; we may again draw attention to the fact that keeping in dilute sulphuric acid for several months did not make the rubber perish (see § 86, page 178). As traces of alkalis have a strong deteriorating effect, it may well be that rubber, to be stable, must naturally keep absorbed a trace of acid, as this is known for other colloids; but this point has not yet been investigated (see § 244 on the acid-content of rubber).

5). The rotting of the coagulum, with the unpleasant smells caused by maturation, is not harmful.

The process of maturation with its prohibitive smell is certainly not attractive; but the inner properties of the rubber are improved rather than injured, and this is also the case when maturation takes place in lower grades.

Of course keeping the rubber under unfavourable circumstances may lead to very marked deterioration (see Chapter XII, especially § 169), but this takes place slowly, and the bad smells of maturation have then already disappeared for some time.

6). It is incorrect to suppose that the less one mangles (either in sheet or crepe), the better it is for the rubber. The rolling is not injurious to the properties after vulcanisation, at least not in the first grades; and in this direction one can go a good bit further than is ever done in practice, without the properties after vulcanisation being affected.

It is quite natural to think that the tearing, twisting, cutting and flattening of the crepe must destroy the coherence and make the rubber less strong.

Nevertheless, this is quite wrong. The fresh, still moist coagulum has so much resistance and tendency to cohere, that it is proof against such attacks. Moreover, when one considers what a much more destructive and reconstructive process the rubber must undergo in vulcanisation, one understands that milling, at most, only affects the rubber very superficially.

As to the practical reasoning that little milling saves time, money and machinery, this is, of course, a sound standpoint, which one must combine with a good finish and exterior of the product. For the rest, a little more or less milling does not affect the rubber (see § 118).

Remilling dry, some months old rubber in the manufacturing process is, of course, quite a different thing to rolling the fresh still moist coagulum, wholly apart from the fact that the old rubber, on large mills, may perhaps become hot, which the wet, fresh crepe on estates never does.

7). Smoking does not improve the inner properties of the rubber.

We treated this point extensively in § 146. One can rather say that smoking injures the inner properties to a small degree, adding foreign substances to the rubber, and thereby diminishing its purity and increasing the loss on washing. Further it may decrease the rate of cure to a not unimportant extent. But on the other hand smoking is very useful in decreasing the susceptibility to mouldiness, and in making the colour more even, and is certainly to be recommended in preparing rubber which contains serum-substances to an amount as in sheet-rubber.

CHAPTER XVII.

VULCANISATION-TESTING.

I. General description of our method of testing and the properties determined by it.

In this chapter we give a general description of the methods used in our testing work, and discuss the significance of the properties which we have so often mentioned in the foregoing pages.

The next chapter will contain technical details on our method of testing, whilst a comparison with other methods will be made in Chapter XIX.

§ 197. Aim of vulcanisation-testing.

The opinion is comparatively wide spread that the elasticity and strength of raw rubber are criteria of its quality in general. It is easy to believe that strong, elastic raw rubber will, after vulcanisation, also have the best properties; but one forgets what a fire-proof the rubber is subjected to during vulcanisation. To be sure there are cases in which the rubber in its raw state shows signs of degeneration which vulcanisation cannot remedy. Thus for instance tacky rubber can never be restored because such rubber is too seriously affected. But ordinarily that which may be detected in the raw rubber by the hand or other means only gives an indication of the momentary condition of gelatination or of the larger grouping of the particles, as it were, which is entirely broken up during the process of vulcanisation, to be rebuilt in a new form. We have more extensively treated this point in § 105, and given some examples of rubber which in the raw state appears brittle, but is strong and normal after vulcanisation, and also of rubber

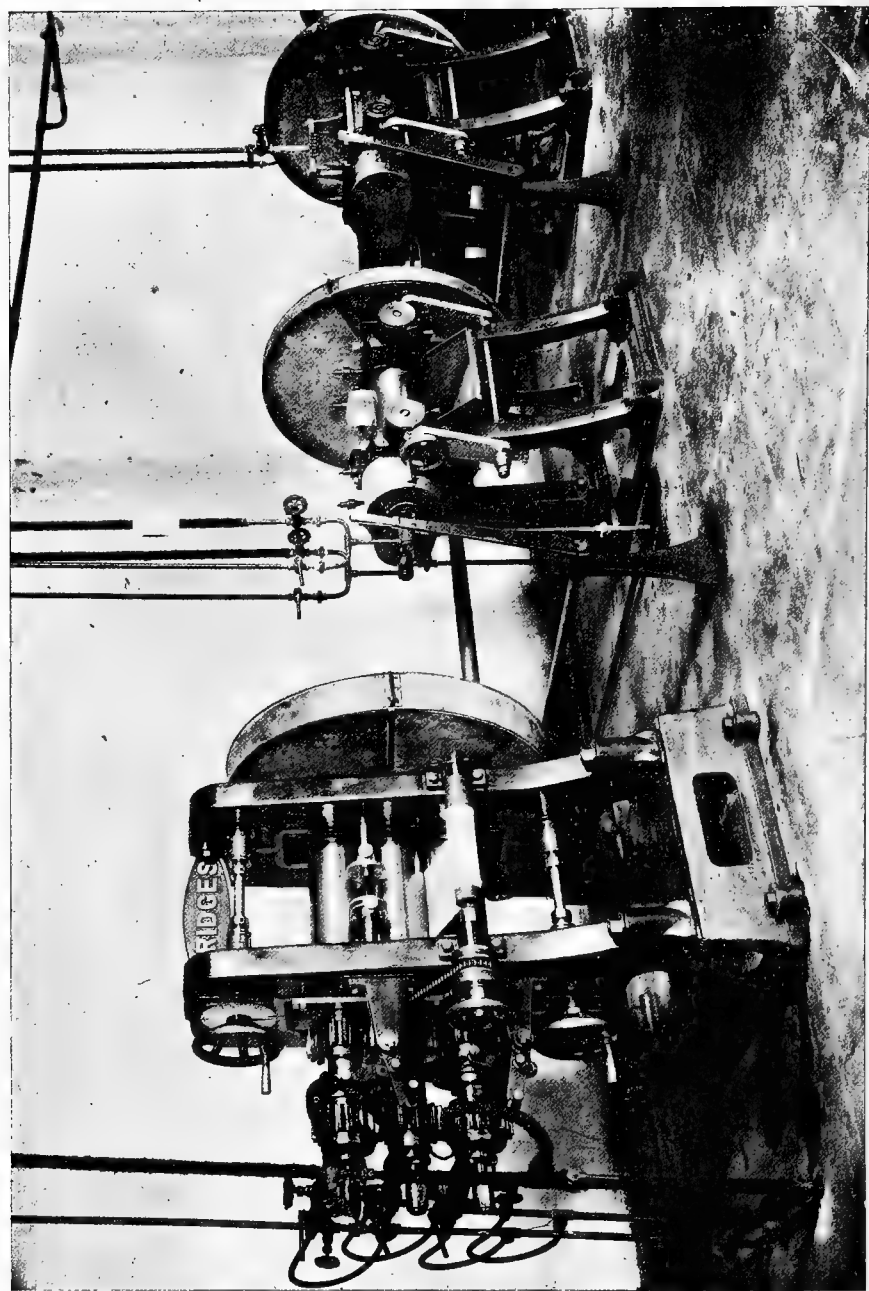


Fig. 10.
Calender, mixing machine and crepeing machine in the Central Rubberstation, Buitenzorg.

which in the raw state seemed very strong and elastic, but proved deficient after further testing.

From these examples it will be clear that the behaviour under vulcanisation can only be judged by subjecting the rubber to this rather drastic treatment itself.

In the following paragraphs we briefly describe the processes through which the rubber passes.

Vulcanisation principally consists of a union of rubber with sulphur. The manufacturer uses many other ingredients, either to give the product certain desired properties or to make the article cheaper. But when it is only a question of judging and comparing the properties of plantation-rubber, mixtures of rubber and sulphur only are preferable, as the properties of the rubber stand out most clearly in such a mixture and eventual differences are sooner detected.

The manufacturer, on the other hand, who wishes to know whether a certain lot of rubber is fit for some special purpose, will use mixtures which will show him the behaviour of the rubber in that special case. By an adequate choice of the mixture the faults and shortcomings of the rubber may often be done away with or at least rendered harmless. This side of the question, however, does not enter into our plan; our aim is only to trace how one can prepare a good uniform plantation-rubber and by what the deviations and faults may be caused. For such purposes one must, of course, choose a method which easily and clearly brings to light the defects, and not one that will in any way obscure them.

§ 198. Mixing and calendering.

Before vulcanisation the rubber must first be mixed with sulphur. Sulphur is not easily incorporated into cold rubber; hence the rubber is first kneaded on hot rolls and brought into a plastic condition. This takes place on the so-called mixing rolls, an ordinary mangle (see Fig. 10) with smooth rolls of 6 inches diameter and 10 inches breadth, which revolve at different speed (in our case 15:22) and which may be brought to the desired temperature by passing steam or water through a pipe in the interior of the rolls. A weighed quantity of rubber is first kneaded on these

mixing rolls, during which process the distance between the rolls is gradually decreased according to a fixed scheme; the rubber is rolled thinner and thinner and gets warm and plastic. The temperature of the rolls at the beginning is 50—55° C, i.e. so warm that one can just touch them with the hand; during the process the temperature rises to about 60° C.

Directly it passes the rolls one sees the rubber becoming warm and weak, it wrinkles between the rolls and takes on a darker brown colour. Pretty white crepe quickly becomes an unsightly brown; of the attractive diamond pattern of sheet nothing is left; and especially for those who are accustomed to judge the rubber always and only according to its exterior, it is surprising to see how it is treated (and in their eyes ill-treated) even in the first stage of testing or manufacture.

After the rubber has become sufficiently warm and plastic by this preliminary treatment, a given quantity of sulphur (7 1/2 parts of sulphur in weight to 92 1/2 parts of rubber) is mixed with it. To avoid loss of sulphur we have adopted the method described by B. J. EATON (*Bull. F. M. S. No. 27 (1918), 27*) for mixing in the sulphur. The warm rubber coming from between the rolls as a thin sheet, is laid on the tray, and the sulphur (contained in a small tin, with holes in the cover, much like a pepper pot) is dusted onto the hot sheet of rubber which is immediately rolled up, so that all the sulphur is included between the folds of warm rubber. This goes on as the rubber comes from the rolls, and finally the roll thus obtained is passed again through the mill. If the sulphur was divided thinly and evenly, it sticks sufficiently to the rubber and nothing is lost. This operation is repeated till all the sulphur is worked into the rubber; remnants in the tin or on the tray are brushed together and added to the mixture quantitatively. This mixture is then further mangled a number of times, during which treatment it is rolled now in this, then in that direction, wound up into a ball, and rolled out again until a satisfactory homogeneous mass is obtained.

The yellow sulphur even at the first rolling melts together with the rubber and soon a kind of dough is formed, that

is finally brought to the desired temperature and plasticity to be milled into a thin even sheet on the calender.

According to the quantity of mixture needed for vulcanisation 55½ to 370 gms of rubber are worked in one operation. The smallest quantity is sufficient to give two rings for testing; a still smaller amount, from which only one ring can be punched, is only used in exceptional cases. For ordinary samples 92½ to 185 gms of rubber are taken; larger batches than 370 gms are preferably mixed in two or more operations.

For plasticising the rubber passes 4—5 times through the rolls; mixing the sulphur it generally takes 2 times, and mixing to a homogeneous mass 10—13 times, whilst the final milling to a roll fit to be passed through the calender takes 3 times. A small batch is finished in 20 times rolling, larger batches in 22—25 times.

Of course the operation is finished sooner for small quantities of rubber and sulphur: small mixes take 8—10 minutes, the ordinary one of 185 gms of rubber takes 12 minutes, whilst large batches such as 370 gms take about 18 minutes.

The calender (see Fig. 10) consists of three vertically arranged rolls, which can be heated in the interior and are so distanced that the rubber-sulphur mixture comes out as an even band of about 2 mM thickness. This band is cut into pieces; three layers one on the top of the other form the plate of somewhat more than 5 mM thickness, which is wanted for vulcanisation. The mixture of rubber and sulphur is exceedingly sticky; even if softly pressed together the layers stick to each other so firmly that they cannot be separated again. When the slab of about 5 mM thickness is ready, it is therefore powdered with talc in order to make it easy to handle and keep.

The properties of this mixture of rubber and sulphur are remarkable. It resembles putty more than rubber; it is plastic and weak, and after a time inserts itself into every fold or unevenness of the objects on which it has been lying; the strength of the rubber has nearly disappeared. The rubber has apparently lost its splendid qualities by this kneading and milling and forms a dough compared to which the

poorest bark- or earth-rubber show a brilliant strength and elasticity. Out of this seemingly mistreated product, by heating to high temperatures, the vulcanised rubber will arise as a phoenix from its ashes.

§ 199. Vulcanisation.

The mixture is now ready for vulcanisation, and pieces may be cut off as desired. Pieces of a suitable size for punching rings later on are put into steel frames and between steel plates in the vulcanising pan (see Fig. 11), in which a hydraulically moved piston presses the pile of plates and frames against the cover. The weak dough, which becomes still more ductile from the higher temperature, is thus forced to assume the thickness and form of the interior of the frames. A small surplus of dough is weighed and put into each frame, and after filling the cavity to the edges and into the corners, the excess is pressed out through small openings or channels (deep 2 mM, wide 10 mM) in the long sides of the frame. This arrangement produces vulcanised slabs of very even properties throughout, and of sufficiently even thickness, which nearly always lies between 4.85 and 5.15 mM, and in far the most cases does not differ more than 0.1 mM from the mean.

For the sake of uniformity rectangular steel frames with 7 by 13 cM inner space, for which 44 gms of mixture are needed, are mostly used; they give a vulcanised slab from which two rings can be punched. Larger frames (inner dimensions 13 \times 19 cM), into which 114 gms of mixture are put, and which give slabs for six rings, are sometimes used. As, however, the heat perhaps does not penetrate into the interior of larger slabs of mixture as quickly as with the smaller ones, or other differences may arise, it is better to adhere strictly to one method of treatment even in such small details; and for obtaining strictly comparable results it is preferable to use frames of one form only.

By steam under pressure the pan is now brought to and kept at the fixed high temperature which is near 150° C (see § 215). It is self-evident that a number of precautions are necessary in order that the results may be as comparable

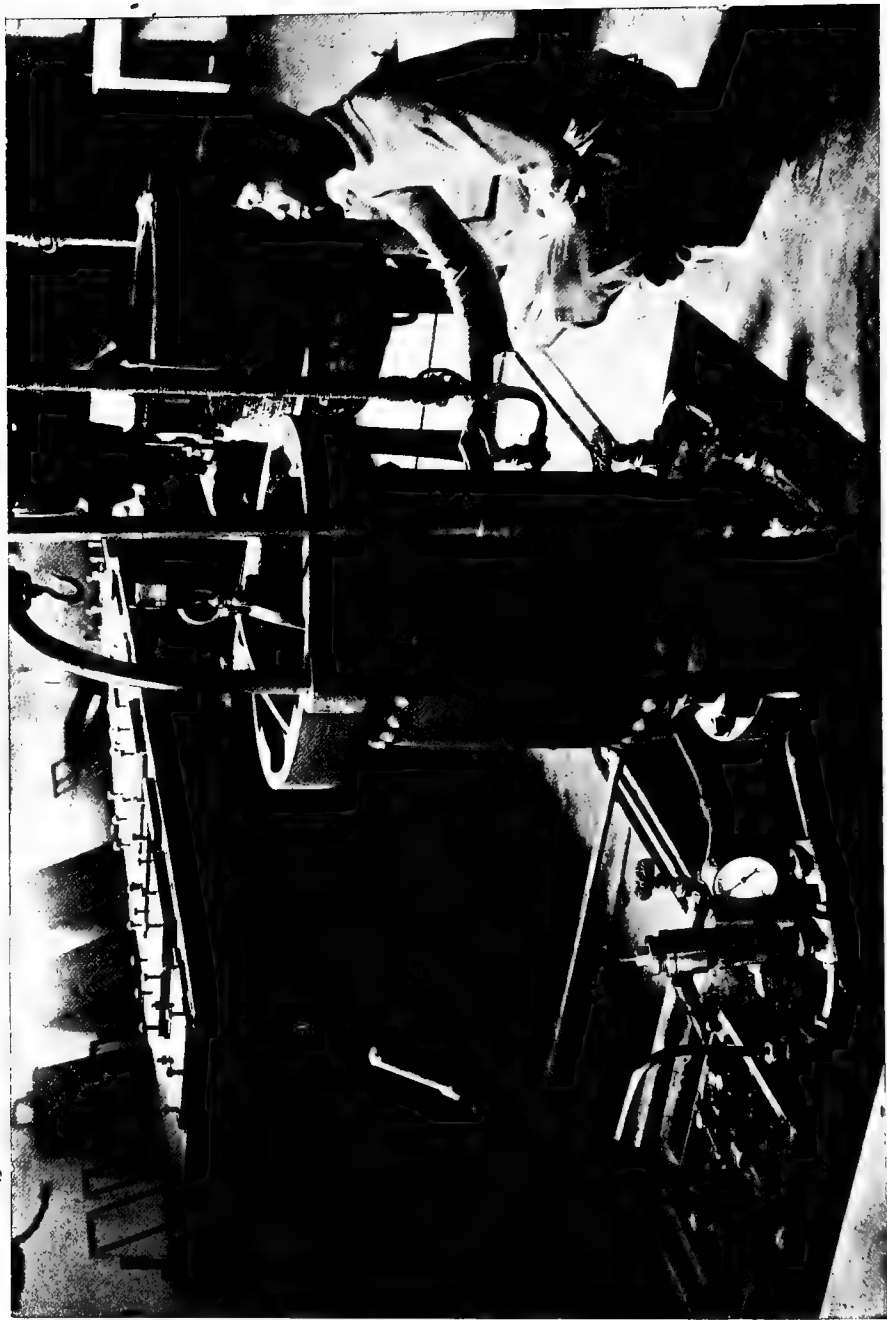


Fig. 11.

Vulcanisation. In the foreground boltless autoclave-press with hydraulic press; native boy controlling the temperature and steam-pressure. In the background vulcanising pan, not in use. On the table moulds used in the vulcanising pan; against the wall, on the left, two steel frames used in vulcanisation.

as possible. The empty pan is always heated to the temperature of vulcanisation before a charge is put in; closing the pan, opening the valves and raising the pressure until the desired temperature is reached must always be done in exactly the same way; blowing off the steam and opening the pan after vulcanisation is also strictly standardised.

In our testing a lapse of less than $\frac{1}{4}$ minute is needed for the interval between opening the steam-valve and reaching the desired steam-pressure; the thermometer, placed in an iron tube which reaches 15 cm into the interior of the pan, the lower part coming close to the pile of plates and frames, must indicate the desired temperature in 3 minutes. After opening the steam-valve for blowing off the steam when vulcanisation is finished, it takes no more than 2 minutes before the plates and frames lie on the table and have reached a temperature of some 80° , at which vulcanisation becomes very slow.

Time of cure is reckoned from the moment that the steam-valve is opened at the beginning to the moment the outlet-valve is opened for blowing off the steam at the end of the operation.

During vulcanisation the temperature and the pressure are continually controlled and kept constant (see Fig. 11), and in order to correct slight deviations which are unavoidable at high temperatures, a piece of one and the same large control sample is added to every load in the pan and a correction is made, if necessary (see § 216). So the rubber-sulphur mixture is heated for a certain time to the high temperature of vulcanisation as evenly as possible; slowly the reactions proceed which change the weak dough into a strong, elastic and extensible vulcanised rubber. The rate at which these changes take place varies for different samples and forms one of the properties which have to be determined. Therefore a trial slab of two rings is generally vulcanised at first for each sample; the result of this trial vulcanisation allows an estimate of the exact time of vulcanisation and a second vulcanisation for the correct time gives us the material for the definite test.

§ 200. Testing the vulcanised rubber.

A great number of instruments and machines have been designed to test vulcanised rubber in different forms and under a number of circumstances. Most of these are destined to determine whether a certain mixture of rubber, sulphur and other ingredients is satisfactory for the special demands of a certain article. When, as in our case, one has only to do with testing and comparing plantation-rubber, such a variety of tests is not necessary. The Central Rubberstation only uses a Schopper testing machine (see Fig. 12) on which rings of vulcanised rubber are slowly and regularly stretched by a hydraulically moved piston, until they break. This stretching gives a good idea of the excellent properties of plantation-rubber; slowly the ring is seen to stretch until it reaches some 10 times its original length or more. A ring of 5×4 mm cross section, that weighs about three gms, carries a weight of 50 to 55 KG.

During the stretching the machine automatically registers the course of the process; when at last the ring breaks, then the weight and the scale on which the elongation is read stand still, so that the final values can be noted. These figures for the breaking point, together with the form of the stress-strain curve, yield the data by which the most important properties of the rubber may be determined.

In Fig. 12 will be seen the testing-machine on which a ring is partially stretched; the weight indicates about 25 KG, the length is about seven times the original; on the registering roll the greater part of the stress-strain curve appears. On the table lie some rings ready for testing; behind one sees the punching machine which produces the rings with its circular knives. To the right the micrometer may be seen with which the thickness of the ring is determined to the hundredth part of a millimetre: the thicker the ring, the greater the strength required for stretching and breaking it; and as not all of the slabs are exactly equal in thickness, they are all measured and a correction is made.

To explain the manner in which rubber is judged we will now first examine the stress-strain curve. Fig. 13 shows a curve

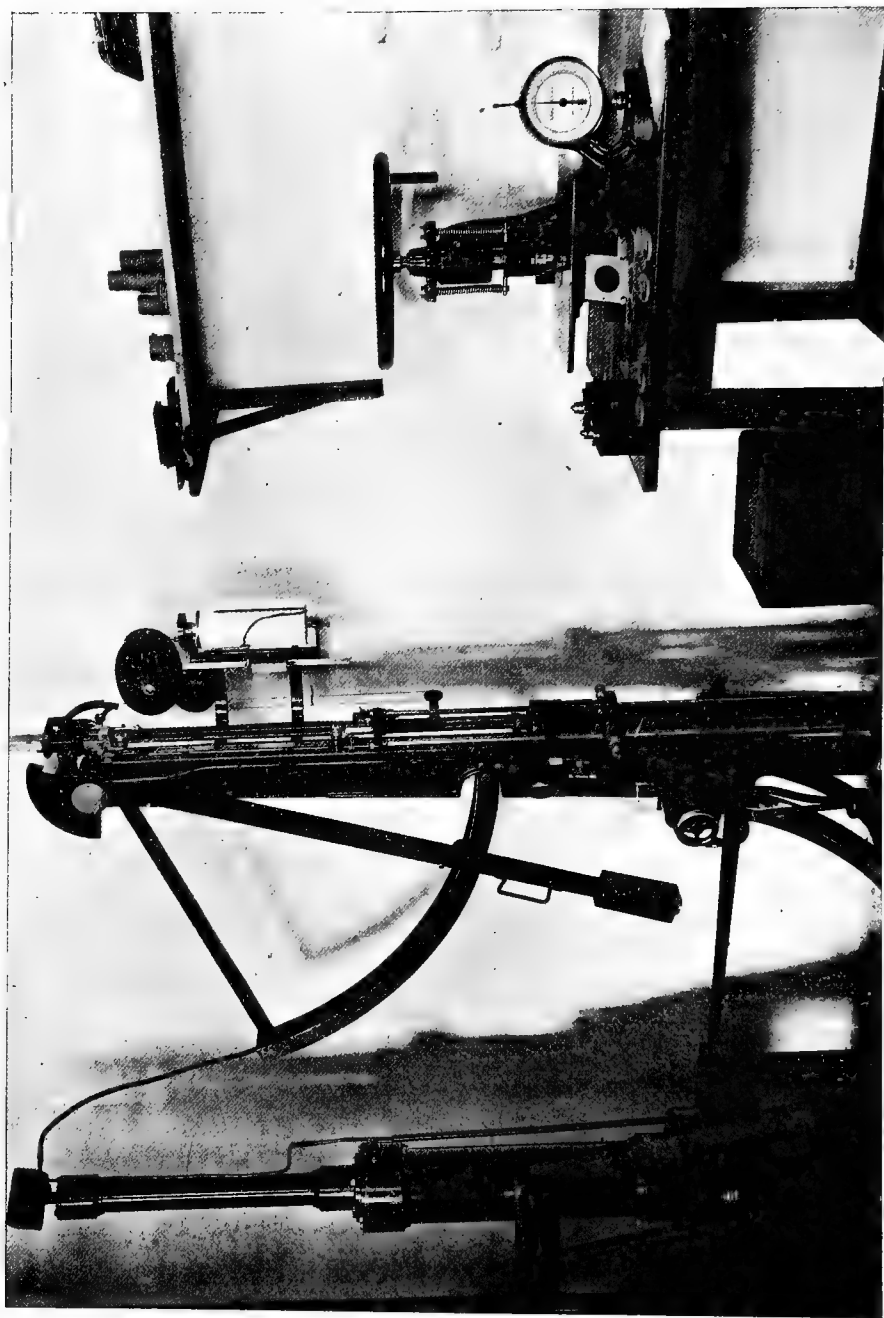


Fig. 12.

Schopper machine for testing rings, with autographic apparatus on which part of a stress-strain curve is visible. On the table punching machine with frames, knives and punched rings, micrometer to determine the thickness of the vulcanised slabs.

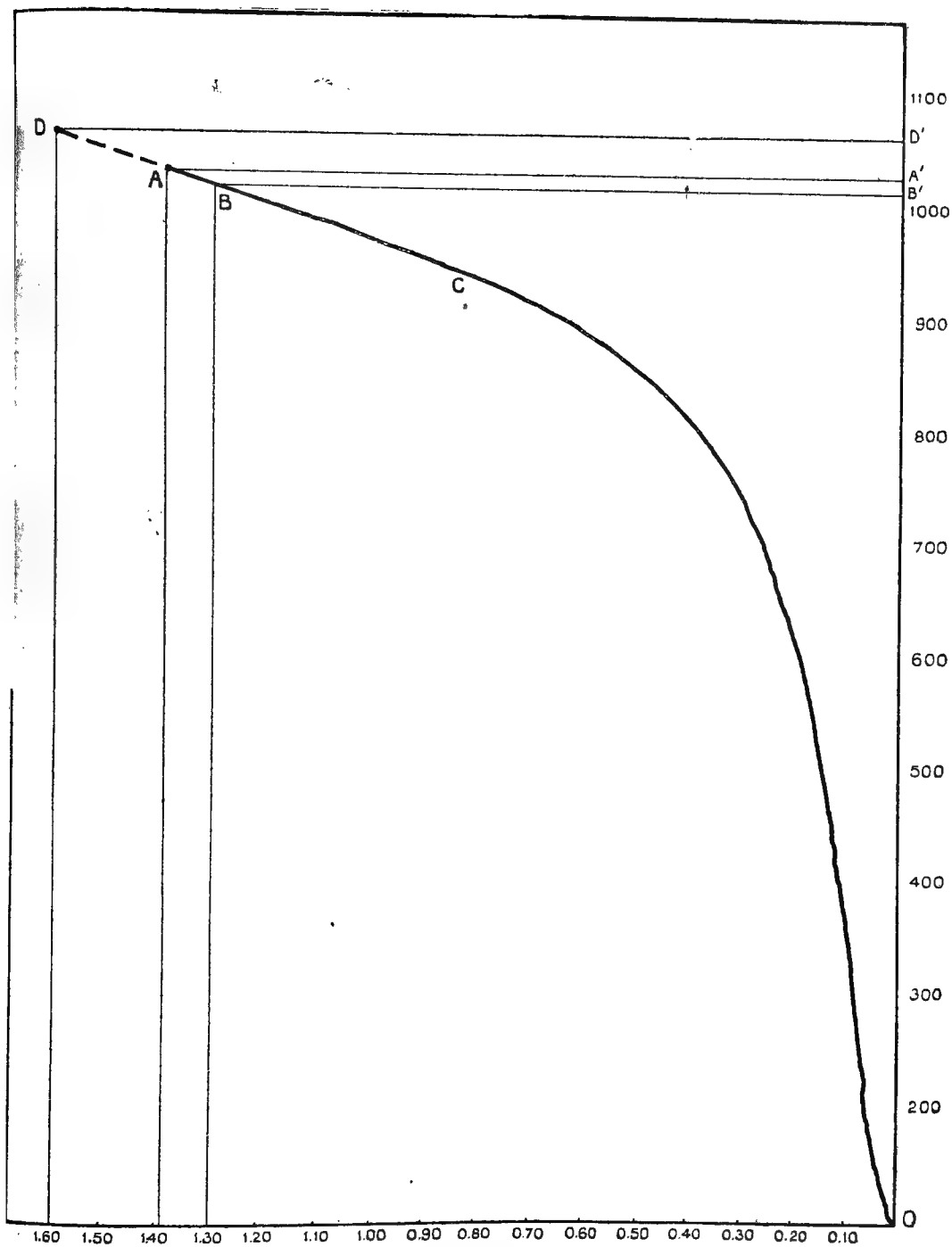


Fig. 13.

• Stress-strain curve as obtained on the Schopper machine.

such as obtained on the Schopper machine. Commencing at O, the curve at first runs steeply upwards; in the beginning the ring stretches easily, without much force being necessary. After the ring has been stretched to 7—8 times its original length, the further stretching becomes more and more difficult: the curve changes its course considerably, and from C onwards runs up regularly with a small but even slope; the upper end of the curve is approximately a straight line.

Following the curve further from C onwards we come to the point A when the ring breaks. A A' is therefore the breaking load, O A' the elongation at break. The position of the breaking point is generally not exactly the same for rings from one slab, but depends upon many minor circumstances. If one examines the broken ring after the test, one usually finds one or more fissures or weak points which should have led to the break if the ring had not accidentally broken in another place. Another ring from the same vulcanised slab might just as well have broken at B, or at another point on the curve, say D. Several rings therefore must be tested in order to determine the mean breaking point. For ordinary samples we take 4 or 6 rings, but in special cases, when very small differences in tensile strength have to be determined, 12 or more, and sometimes even 30—50 rings are tested.

The form and position of the curve vary with the state of cure of the rubber. Fig. 14 depicts the stress-strain curves for one mixture of rubber and sulphur, vulcanised for different lengths of time. With a vulcanisation of 60 minutes the curve runs up steeply and only shows a slight inflection; the strength necessary for breaking is comparatively small (0.49 KG per mM): the vulcanised rubber is weak though very resilient and elastic. If vulcanisation is carried on further, then more strength is required to bring the rings to the breaking point; with each increase in time of cure the rubber becomes stronger, until a point A is reached which shows a maximum of tensile strength.

After longer cures the tensile properties fall off and the product soon becomes brittle, so that it easily snaps in two when stretched by hand; over-vulcanisation has then taken place.

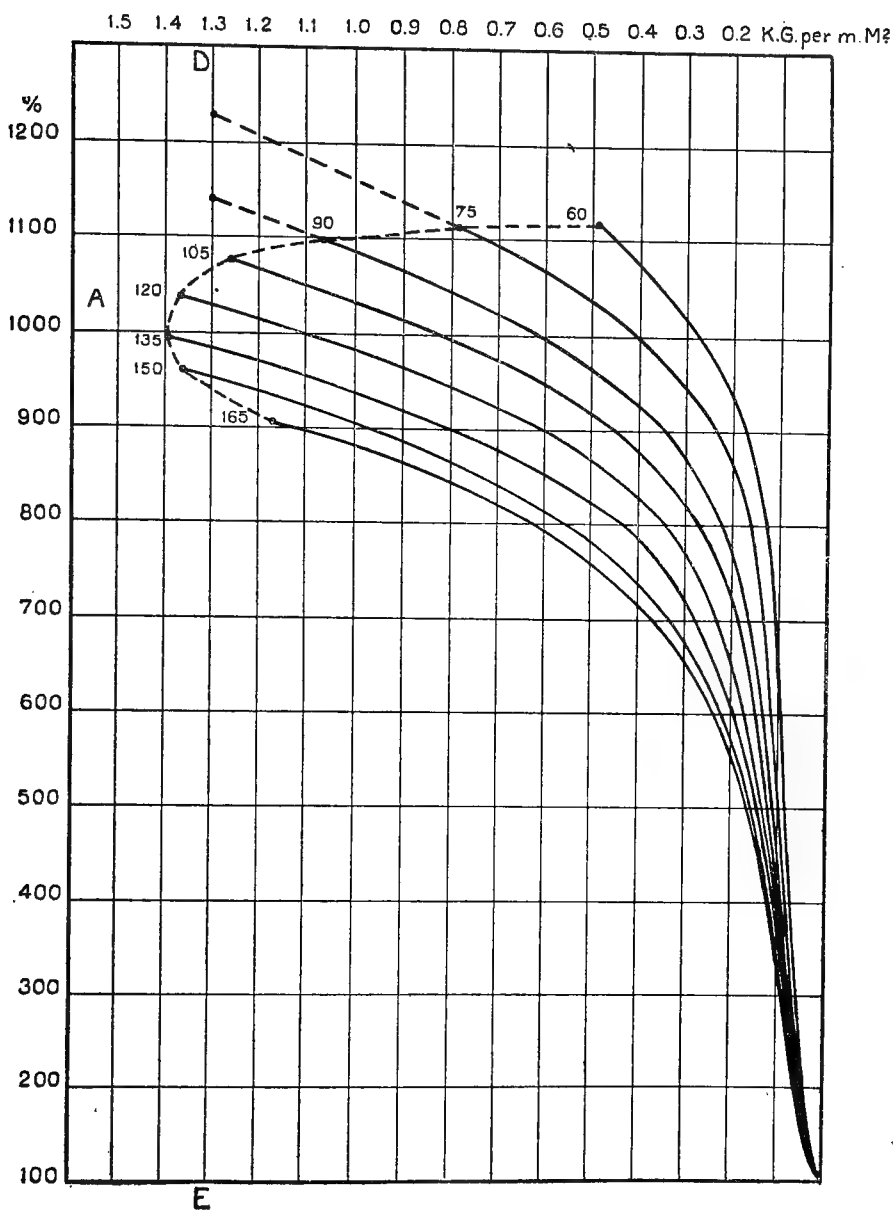


Fig. 14.
Stress-strain curves and breaking points for one sample of rubber, cured for increasing times.

When increasing the time of cure, the position of the curve and of its endpoint, the breaking point, therefore gradually change. As the successive curves for one sample have definite forms, the breaking point would be sufficient to fix the whole curve. The fortuitous character of the breaking point, however, makes it little fit for this purpose. It is still the custom with many investigators to mention as the only figures from their tests the breaking load and the elongation at break; but these figures do not easily give a correct idea as to what curve has been found, and where the breaking point lies on that curve. Only when plotting breaking loads and elongations on squared paper, can the relative positions of different breaking points be judged. For instance, from the figures alone it would not easily be seen that a breaking load $D D'$ (Fig. 13) combined with an elongation $O D'$ mean a point on the same curve as $B B'$ combined with $O B'$; and for other figures one cannot deduce whether they lie on a higher or a lower curve, without plotting breaking load against elongation. Still, the position of the curve is an important point, as it changes with increasing cure; it has certainly to be taken into account in judging the results. The position of the curve is best expressed by its length at a fixed load, or by its load at a fixed length: such figures give a direct reading of the vertical or horizontal distance between different curves, and show at a glance which curve lies higher, and how large the difference is.

In reading the properties of rubber from sets of curves as just described, different points have to be taken into account. In our testing we refer to:

- 1) the time of cure necessary to reach a certain curve, or the position of the curve reached after a certain cure;
- 2) the form of the curve;
- 3) the endpoint of the curve.

In practical testing it is, of course, impossible to determine the whole set of curves for every sample; especially an accurate determination of the endpoints would necessitate the testing of a large number of rings, as the figure for breaking load is more or less accidental.

The testing can be simplified by taking into account the fact that the curves for increasing times of cure change regularly in position and form, and for each sample in a similar manner. Though exact data for the whole range of cures are still insufficient, it is clear enough that certain laws or relations exist, and that it is allowable to draw conclusions on the whole set of curves from one or a few states of cure. The mathematical data which would make this possible are, however, still imperfectly known and only worked out for certain limited regions of the whole field.

In Chapter XIX we will discuss the methods used by different investigators to express the properties which can be read from such a set of curves; here we only describe the properties determined in our method of testing and often mentioned in the first part of this book.

As standard state of cure we have chosen a cure in which the stress-strain curve at a load of 1.30 KG per mm^2 shows a length of 990 (elongation 890), taking the original length as 100. The curve in Fig. 13 lies somewhat higher than the standard (length at 1.30 KG 1012 %); in Fig. 14 the standard state of cure is approximately represented by the curve for 135 minutes. The standard position of the stress-strain curve brings ordinary smoked sheet and crepe approximately to the maximum of tensile strength; and as the maximum is, using our mixture, rather flat (compare § 205 and 223), this has the advantage that curves which deviate slightly from the standard may be taken as giving the tensile strength for standard cure without further correction. This figure for tensile strength practically coincides with the maximum tensile strength for the bulk of plantation-rubber; only in very inferior lower grades our standard cure gives a lower tensile strength than the maximum (compare § 205).

The position of curves near this standard state of cure is best and most sharply determined by their vertical distance, as the curves themselves in this region run nearly horizontal.

We have chosen a load of 1.30 KG as one which is just surpassed by all first grade samples, and reached or nearly

reached by most of the lower grades, so that in determining the load at 1.30 KG from the figures for breaking point (see § 220), the error can never be large. The figures for length at 1.30 KG show at a glance which curve lies higher or lower, and how large the distance is.

Of course, in special cases other vertical cuts can be made through the bundle of curves, and comparisons between the length at 1.20 KG or 1.10 KG are useful, for instance for rubber with very low tensile strength, in which the extrapolation (prolongation of the curve) to 1.30 KG would be too uncertain.

Having once adopted this standard state of cure, the *rate of cure* is simply expressed by the time of cure needed to reach this standard under our conditions of curing and testing. A sample sent in for testing is subjected to a preliminary cure, that is a slab of two rings is added to any charge that will be cured for a suitable time. The position of the curve produced by this preliminary cure is determined in the ordinary way. If it differs too much from the standard, a second trial can be made; but generally the first trial gives sufficient data to judge of the *standard time of cure* (compare § 203), to which slabs for 4—6 rings are then subjected. For ordinary testing curves which differ not more than 15 units in length at 1.30 KG from the standard curve give sufficiently exact data; for very minute investigations the cure may be repeated. An ordinary estate-sample, sent in for testing, generally necessitates only two cures, one trial of two rings, and one final of 4—6 rings; 185 gms of rubber with 15 gms of sulphur are weighed and give sufficient mixture for 8 rings.

The *tensile strength* mentioned in our tests is the breaking load in KG per mm^2 at standard state of cure; figures for curves in the neighbourhood of the standard curve are taken without correction, as the maximum is rather flat, and a difference of 15—20 units in length only means a decrease in tensile strength of 0.01—0.03 (compare § 205), which is within the limits of error when the breaking load is only determined from 4 to 6 rings.

The *slope* is determined also for the standard state of cure.

To ensure as much as possible uniformity in expressing the methods of testing, we have adopted the formula of PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 51 (1916), 505; J. S. Ch. I. 38 (1919), 347 T), who arbitrarily express the slope as $0.4(\text{length at } 1.04 \text{ KG} - \text{length at } 0.6 \text{ KG})$. This, therefore, is not the slope of the upper, straight end of the curve, but the slope of a secant in the strongly curved shoulder of the curve. See for further details § 221.

The slope changes somewhat for increasing times of cure (see § 221); but as the stress-strain curve is never a completely smooth curve and always shows small oscillations and irregularities (compare § 218), the determination of slope is liable to an error of some 0.5, and the slope of curves near the standard state of cure may, for all practical testing, also be taken.

The slope of different samples of rubber differs, and the form of the stress-strain curve is therefore not exactly the same; but the difference, for ordinary samples, is small and can only be found after exact comparison. Nevertheless it is well to draw attention to the fact that our method of testing cannot be called a standard curve method; the point showing a length of 990 % and a load of 1.30 KG, by which the standard state of cure is fixed, might be called the *standard point*.

Having now given a general description of our method of curing and testing, and defined the three properties—tensile strength, slope and rate of cure—determined therein, we will in the following paragraphs give some further details on these properties. Rubber testing never gives absolute values; even if the principal factors—such as percentage of sulphur, temperature of vulcanisation, type of testing machine—are the same, minor differences influence the results to such an extent that it will probably be impossible ever to reach strictly comparable figures in different institutes. Testing results should never be judged on their absolute value, but always be compared with the average or standard figures obtained by the same method (see also § 228); to allow of a comparison, we will summarise in

the following paragraphs the figures obtained in our testing of hundreds of samples of plantation-rubber in the course of years.

The numerical values being fixed, it remains to be discussed which factors in preparation influence them, and what may be deducted therefrom as to the nature of the property in question. Prescriptions as to methods of preparation have already been given in Chapters IX, X and XIII.

§ 201. Tensile strength.

The tensile strength of a large number of estate-samples, tested during the years 1917—1919, is depicted in Fig. 15; the average figures and the normal values for first quality crepe and smoked sheet have already been mentioned in § 132, 154 and 155, whilst figures for the different types of lower grade may be found in Chapter XIII. Figures mentioned elsewhere in this book, or in our Communications, can be judged by sketching them in Fig. 15; the normal values for first grade rubber are 1.35 to 1.45, whilst in the lower grades tensile strength may decrease to 0.80, or even to much lower figures such as 0.20, when particles of dirt are present.

On the whole a high figure for tensile strength is, of course, preferable. For a number of articles, which are not subjected to any important extension, a somewhat higher or lower value for tensile strength probably will not play any important role, and in others (such as erasers, floor-matting etc.) the manufacturer intentionally adds substances which largely diminish tensile strength, whilst giving other desired properties to the finished article. Be this as it may, the aim in the preparation of plantation-rubber must always be to obtain a high, or at least a good average figure for tensile strength.

The factors which influence tensile strength are not completely known; the following points may be brought together from the foregoing chapters.

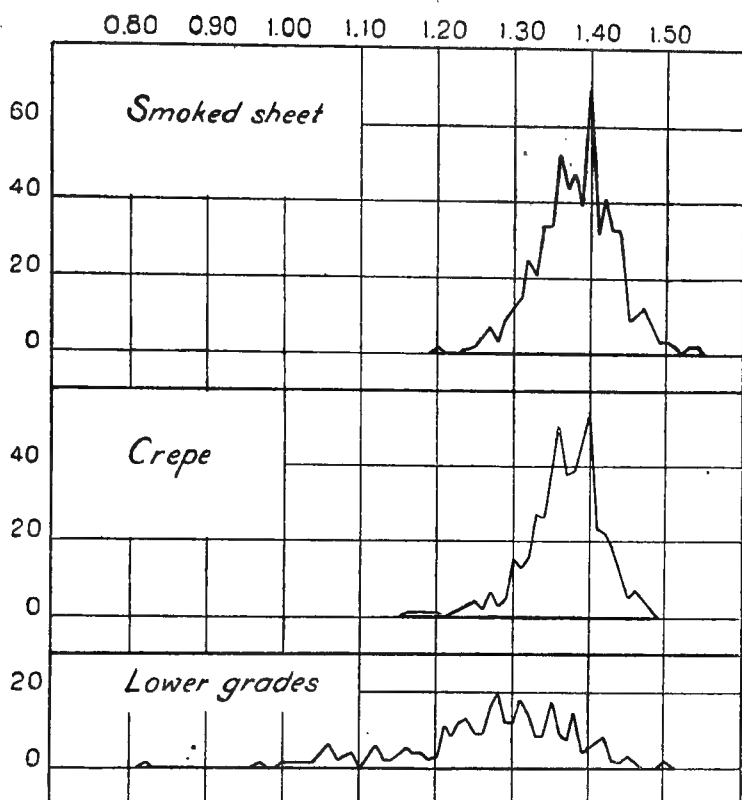


Fig. 15.

Tensile strength of 1415 samples from the output of a large number of estates, tested in 1917—1919.

- 1) rubber from very young trees often shows a low tensile strength; in trees of the ordinary tapping age there are, however, no indications that the tensile strength of the rubber increases with age (see § 24).
- 2) a prolonged period of heavy drought may, in all probability, cause a decrease in tensile strength; strictly conclusive sets of figures are, however, not yet available (see § 20).
- 3) tapping pollarded trees may probably result in a rubber of somewhat lower tensile strength, but data are still scarce on this point (see § 36).
- 4) some coagulants, such as sulphuric acid and alum, when used in excessively large quantities, cause a

decrease in tensile strength (which, however, partly originates in the decrease in rate of cure, see § 204). Compare § 86, 88 and 91.

- 5) partial coagulation gives a first clot with a lower tensile strength and another composition than the rest, or than coagulation as a whole (§ 176).
- 6) heat, namely rather high temperatures such as above 85° C, or above 70° C by long duration (which temperatures are seldom or never reached in drying or smoking sheds on estates) may influence the tensile strength (see § 125, 145 and 165).
- 7) organisms that cause spots on crepe may, in certain cases, give a decrease in tensile strength (see § 168).
- 8) other organisms may attack the rubber, for instance when kept on or in the soil, and completely deteriorate it (see § 183).
- 9) sunlight, after sufficiently long exposure, completely liquifies the rubber; the tensile strength is damaged long before that (see § 164).
- 10) copper salts, which cause tackiness, diminish the tensile strength (see § 169).

Probably there are other factors which may affect tensile strength; but as a whole it will be seen that the cases enumerated above are rather exceptional. In the ordinary course of rubber-preparation there is nothing that affects the tensile strength of the product, which property is to a large degree insensible to the ordinary variations and differences in estate-practice. In this respect a striking contrast exists between tensile strength and rate of cure, which latter property is influenced by nearly every change in preparation (see § 203). It will be noted that amongst the factors enumerated above even „excessive milling” fails; in § 118 we have seen that milling the fresh coagulum is without influence on tensile strength. Very excessive dilution with water might perhaps be added to the above list (see § 64); but in that case the large decrease in rate of cure is a cause of decrease in tensile strength, and data are not yet sufficient as to whether this factor alone may wholly explain the decrease observed in tensile strength (compare § 204).

In reviewing the cases mentioned above we clearly distinguish two groups of factors affecting tensile strength (excepting No. 4, in which case probably the decrease in rate of cure is the principal, if not the sole cause). The first group comprises cases 1—3, in which the tree is affected, and probably produces a rubber-hydrocarbon of somewhat inferior properties; the second group, cases 6—10, is characterised by a deterioration of the rubber, accompanied by oxydation or decomposition.

We therefore come to the conclusion that tensile strength largely if not wholly depends upon the properties of the rubber-hydrocarbon itself, which is immune against the greater part of the variations that may occur in the latex or the methods of preparation, and is only affected in exceptional cases.

Still, as will be seen from Fig. 15, the variation in tensile strength in estate-samples is rather large. In the lower grades, dirt and impurities play an important role, whilst in such cases a beginning of decomposition will also often be the cause of low values. In the first grades, dirt or dirty water may in some cases cause a decrease in tensile strength (see § 40 and 119); taking young plots of trees into the tapping round is probably one of the more common causes of a somewhat low figure, whilst a heavy and prolonged drought may be suspected in other cases. Still, the rather frequent occurrence of a somewhat too low tensile strength is an indication that there are other, still unknown, factors at work. Since these are not to be found in preparation, one has to look for them amongst the factors that influence the latex. Strain of seed, soil, climate may be named, but only as possibilities, as no data are available giving sufficient proof in any direction.

In this connection it is interesting to mention that we have often noted a marked and regular difference in tensile strength for series of samples from different estates, received and tested during the same period, that is under strictly comparable conditions. As an example the following figures for samples of first quality crepe, received during the year 1917, may serve:

Estate	Number of samples	Tensile strength	
		Limits	Average
A	6	1.37—1.45	1.42
B	12	1.37—1.45	1.40
C	11	1.35—1.47	1.41
D	8	1.35—1.42	1.37 ¹ / ₂
E	7	1.30—1.38	1.34

The first two estates have an excellent tensile strength throughout, the figures for nearly all samples being above the average; the last named estates only in one sample (1.38) reaches the average, all other samples showing low figures. No reason can, as yet, be given for these differences, but the fact itself is interesting, as it indicates the importance of tensile strength tests, and at the same time the difficult position of the adviser, who has to state the deficiency without being able to take away or even point out the cause.

§ 202. Slope.

Values found for slope in more than twelve hundred estate-samples of different grades are reproduced in Fig. 16, which illustrates the figures already given in § 132, 154 and in Chapter XIII. Whilst for first quality smoked sheet and crepe the range is rather small, the lower grades may show very high figures. Very characteristically its author has called this property „type”; it is indeed typical for the grade or quality in a wider sense. In the lower grades the figure for slope is a better guide than tensile strength, which is so often influenced by particles of dirt etc. High figures for slope, such as 42 and more, generally indicate a rubber which on keeping becomes tacky. Whether a difference between, say, 35 and 38 in the first grades is of any practical importance to manufacturers or for the properties of the rubber in general, still remains to be seen.

The real nature of the property which finds its expression in the slope of the stress-strain curve is not yet cleared up. The following factors were found to have an influence:

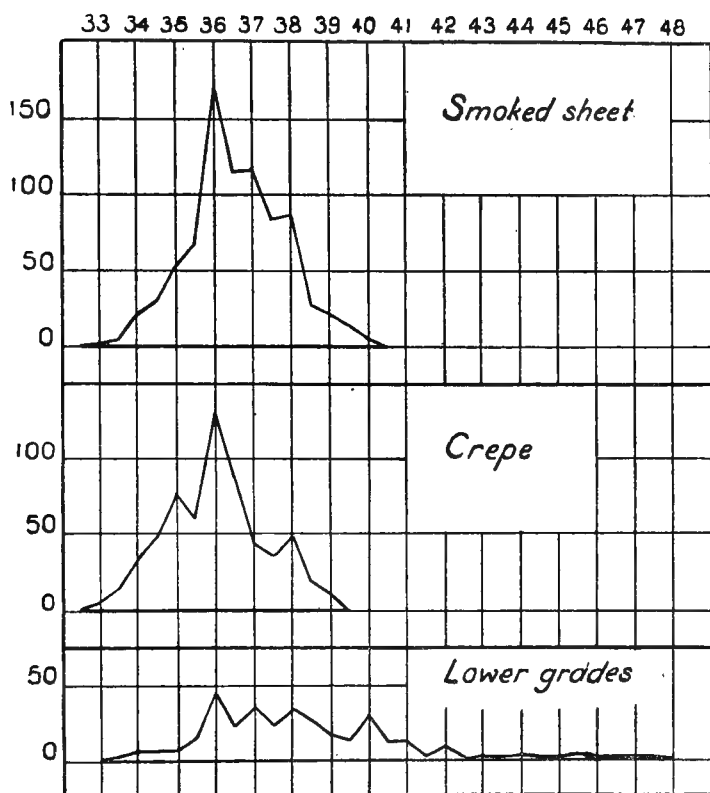


Fig. 16.

Slope for a large number of samples of smoked sheet, first quality crepe and lower grades, tested during 1917—1919.

- 1). The slope becomes greater (the rubber less resistant to stretching) by continued tapping after opening a tapping cut on trees that have had a rest (§ 29).
- 2). The slope becomes greater by applying heavy tapping systems (§ 32).
- 3). The slope decreases by adding sodium sulphite or sodium bisulphite to the latex, and in coagulation with sulphur dioxide (see § 44, 48 and 52).
- 4). Coagulation with alcohol gives an increase in slope (§ 99).
- 5). Maturing the fresh coagulum gives a decrease in slope (§ 108).
- 6). Strong heating of the fresh, still wet coagulum may cause the slope to increase (§ 120).

- 7). Lower organisms, which cause spots on crepe, may produce an increase in slope (§ 168).
- 8). Copper salts, causing tackiness, give an increase in slope (§ 169).

On the other side the simple addition of inert substances such as gypsum or talcum, in amounts up to 1 %, leaves the slope unaltered, whilst the percentage of sulphur used in vulcanisation (5–10 %), is also without influence on this property (compare § 223). This proves that a simple mechanical admixture or „dilution” of the compound is not the cause of a decrease in slope; and though the above named cases do not yet clearly show which property is responsible for changes in slope, it would seem that decomposition or oxydation products of the rubber play a certain role, more than the serum-substances or their decomposition products. Further research into the deeper nature of this property will, however, be necessary to clear up its real significance.

In our testing the slope is of importance also because a parallel exists between this property and permanent set (see § 207). Slope can be determined with the same rings and curves used in the tensile strength test, which spares the time and material otherwise used in permanent set tests.

§ 203. Standard time of cure.

The figures found for the estate-samples tested during the years 1917–1919 are reproduced in Fig. 17. They clearly illustrate the points already discussed on former occasions (§ 132, 154, 156 and 175), viz. that smoked sheet shows a greater rate of cure than crepe, but also a greater variability on this point; and that the figures for the lower grades vary over the same range as those for the first grades.

The extreme figures are 65 and 150 minutes; if special cases were included, the range of variability would be still greater, figures such as 30 and 40 minutes being found for matured rubber, whilst certain coagulants (sulphuric acid, alum etc.), when used in large excess, may increase the time of cure to 180 or even 240 minutes.

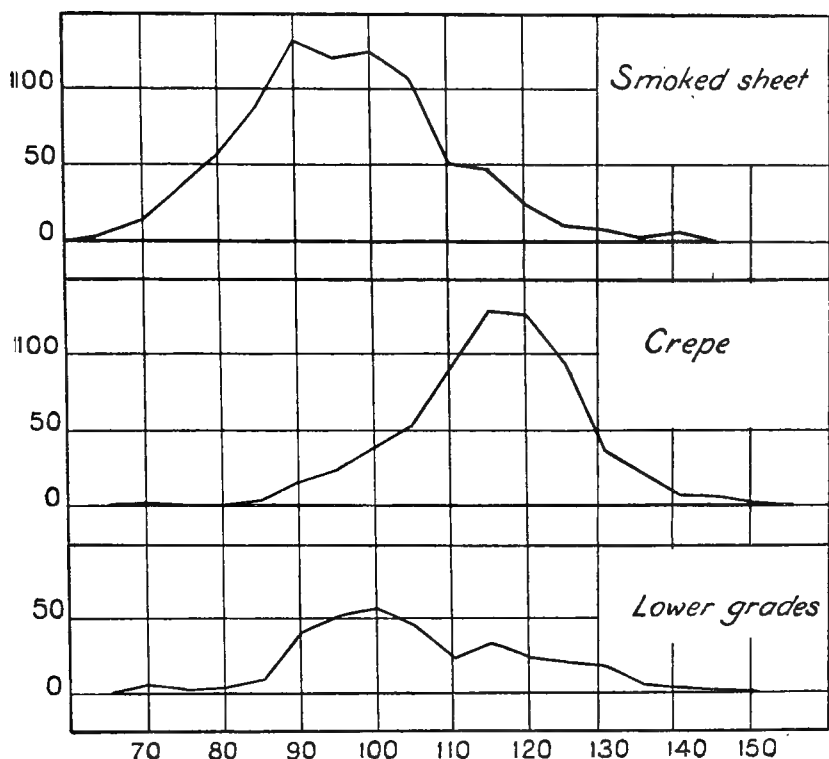


Fig. 17.

Standard time of cure for nearly 1800 samples from different estates, tested during 1917—1919.

On the way in which figures for rate of cure have to be judged opinions have differed largely. Many authors regarded an increase in rate of cure as an advantage, as it spares the manufacturer time and steam; and they carried this principle so far as to proclaim every increase, even of 5 minutes, in time of cure as an indication of a rubber of better quality, or at least of a more valuable product. Against this standpoint it has in the first place been argued that differences in rate of cure observed in a mixture of rubber and only sulphur are not necessarily found again in technical mixings, and especially not if accelerators are added. It may further be safely assumed that a small increase in rate of cure is not of so much importance to manufacturers as uniformity in this property in lots of one type of rubber.

It probably makes little difference to manufacturers whether smoked sheet, in bulk, vulcanises in 90 or in 100 minutes, but they have repeatedly voiced the wish that lots from different origin show as little variation in this respect as possible. The aim in preparation on estates must therefore be to evolve methods which ensure the highest degree of uniformity under the different circumstances prevailing on estates. Samples should be judged not on the absolute value for time of cure, but on its deviation from the general average, whilst methods of preparation should be so developed that exceptions and large deviations are more and more avoided, and that the unavoidable variability is confined within more and more narrow limits. *In rate of cure not high figures, but average figures are the best.*

As we showed in the Introduction (page 3), it would be better not to include rate of cure amongst the properties determining the quality of rubber. Quality, in the strict sense of the word, is expressed by such properties as tensile strength or slope. A defect on these points cannot be remedied, or better a rubber with inferior tensile strength or slope remains inferior throughout. A deviation in rate of cure may, on the contrary, be remedied by an adequate choice of the mixture, by using accelerators etc. Abnormal rates of cure are troublesome and undesirable; but they do not mean a real and irreparable inferiority.

Variations in rate of cure of plantation-rubber are principally caused by the non-rubber substances which evidently, as catalysts, influence the reaction between rubber and sulphur. These substances may be grouped under the following heads:

- 1). the substances present in the latex as it exudes from the tree.
- 2). the chemicals added in preparation (water, anti-oxydants, coagulants etc.).
- 3). the substances that are formed in the latex or the coagulum by interaction or decomposition of those named under 1 and 2.
- 4). smoke-constituents absorbed during smoking.

Whether the rubber-hydrocarbon itself has an influence on the rate of cure, is still unknown. Assuming that very young trees indeed produce a rubber-hydrocarbon of somewhat deviating composition (see § 24 and 201), then the larger rate of cure of rubber from such trees might as well be explained by such a difference in the rubber-hydrocarbon, as by differences in the non-rubber substances. Further research alone can decide such points.

PH. SCHIDROWITZ (I. R. J. 60 (1920), 161) again draws attention to depolymerisation as a possible cause of the increase in rate of cure found when slow curing samples prepared with sulphuric acid are stored (compare § 86, page 178).

That rate of cure is largely influenced by many factors, has been extensively shown in the foregoing chapters. In contrast to tensile strength and slope, which are left unaltered by the majority of differences met with in estate-practice, rate of cure is affected, be it to a small extent, by nearly every change. It would lead us too far to enumerate all cases treated in the foregoing chapters of this book; we restrict ourselves to a short review of the principal points.

That differences in composition of the latex — due to differences in the trees themselves, or to the treatment to which they are subjected — are a common cause of variability in rate of cure, was shown in Chapter II. In fact, the differences are so general that bulking the latex is the only means of attaining a certain degree of uniformity; and still, bulked latex from different groups of trees, estates etc. shows a rather large variation. The more the methods of preparation on estates become standardised, the more the differences in composition of the latex will stand out as a cause of variability in the product. It may be safely assumed that the general adoption of mild tapping systems in later years has done much to ensure a more uniform product; but other factors, such as strain of seed, age of trees, soil, climate, general condition of the plot etc, cannot be standardised at will and must continue to be a cause of variability, unless a method of preparation is found which neutralises differences from these sources.

That the variation in rate of cure, caused by factors under this head, is rather large, was shown in Fig. 2 and § 37.

Abnormally slow curing rubber with times of cure such as 150 minutes may be obtained when starting tapping after a period of rest; very rapid curing sheets are sometimes produced by young plots, and the differences in rate of cure caused by factors falling in this group cover the whole range of variability found in estate-samples.

The influence of foreign substances added to the latex was treated in Chapters III, IV and VI. The use of these substances is in practice always restricted as much as possible, be it only from reasons of economy, and the deviations in rate of cure caused by their use are generally small. Excessive use of formalin may give a marked retardation, but otherwise the use of water in diluting and standardising the latex is probably the factor which gives the largest differences in practice, but which can be easily standardised for every estate. Still, these factors explain to a certain degree the minor deviations found in estate-samples; the use of an anti-coagulant in times when this becomes necessary, the somewhat increased dose of acetic acid during wintering, and such changes will often cause a certain degree of variability.

The third group mentioned above comprises not only the large increase in rate of cure found after complete maturation (§ 108), but also the numerous cases in which decomposition does not proceed so far. We have many times drawn attention to this beginning of maturation, and have reviewed a number of cases in § 153, where the larger variability of sheet-rubber as compared with crepe was explained. The ideal would, of course, be to standardise methods of preparation to such a degree that this whole group of factors is excluded; but in practice this is, at present at least, impossible. Factory equipment, local circumstances such as site of factory, distances over which the latex has to travel, labour questions and many others, which affect the economic side of preparation, often necessitate a certain course being chosen to the exclusion of others. Unavoidable changes of circumstances—even pleasant ones, such as, for instance, an increase in production, which temporarily makes the drying space insufficient—are further disturbances in practice. A certain degree of variability may,

in most cases, be expected from this source, but the aim must be and is to avoid it as much as possible.

The fourth group—extraneous substances absorbed during the smoking process—was treated in Chapter X and may add to the variability found in smoked sheet.

§ 204. Interdependency of properties.

In testing a substance with such complicated properties as rubber one must, of course, try to determine as many independent properties as possible. Now tensile strength and slope, as we have seen in § 200, change with increasing state of cure; in testing they must be so expressed that they represent, as much as possible, independent characteristics, which are comparable for different samples. In how far this may be reached in different methods of testing will be discussed in Chapter XIX; here we will only discuss in how far there is an interdependency of the different properties in our method of testing.

Tensile strength is made as much as possible independent of *rate of cure* by bringing every sample to a standard state of cure, regardless of the time it has to be cured to reach this state of cure; tensile strength is determined for this comparable state of cure. Still, a certain influence of rate of cure cannot wholly be avoided in this manner: samples which require a long cure are somewhat damaged by the longer heating, and a longer time of cure means a small decrease in tensile strength. This might, of course, be avoided either by applying a correction in tensile strength, or by adding an accelerator so that every sample is cured for the same time (see § 226). Such a method has, however, not yet been further developed, and we have for the present to content ourselves with uncorrected figures for tensile strength.

We have made special experiments in the following way to prove that a small difference in tensile strength is caused by the time of cure. Crepe was left in the wet state for one to three days, so that a beginning of maturation set in, and the rate of cure increased; sheet from the same latex was soaked for 1 to 5 hours in water, which extracts serum-substances and decreases the rate of cure. It is very improbable that

such treatments as simply keeping or soaking in water affect the tensile strength. From a number of experiments the values were calculated for crepe vulcanising in 80 and 105 minutes, and for unsmoked sheet with the same times of cure. The results were:

	Crepe	Sheet	Average
Time of cure 80 minutes	1.46	1.45	1.45 ⁵
" " " 105 "	1.40 ⁵	1.42 ⁵	1.41 ⁵

so that no distinct superiority for sheet-rubber appears; the longer time of cure has in these experiments caused a small decrease in tensile strength for both types.

Keeping this before our eyes, it may be asked in how far the differences in tensile strength mentioned in the first part of this book are intrinsic, and in how far they are caused by differences in rate of cure. The following cases are interesting.

1) For smoked or unsmoked sheet and crepe, prepared from the same latex, the figures mentioned in § 155, page 333, give a difference in tensile strength of 0.01 to 0.05 for a difference in time of cure of 3 to 31 minutes, so that, in connection with the above average difference of 0.04 for 25 minutes, the greater tensile strength of those sheets may be wholly explained by their greater rate of cure.

The difference between smoked sheet and crepe from estates was given in § 155 as:

	Tensile strength	Standard time of cure
Smoked sheet	1.384	96.3
Crepe	1.367	115.7

In connection with the above it may be assumed that this difference of 0.017 in tensile strength is caused by the difference of 19.9 minutes in time of cure, so that the intrinsic tensile strength of sheet and crepe is the same, in

good accordance with other facts proving that the tensile strength of neither grade is affected by any stage in its preparation.

2) Crepe from matured rubber shows the following figures :

	Tensile strength	Standard time of cure
Spontaneously coagulated	1.41	50
Coagulated with acetic acid	1.41	75
Ordinary crepe	1.385	100

In this case also a somewhat smaller tensile strength for the slower curing type is observed. The figures are not strictly comparable, the crepes not having been prepared from the same latex; a real superiority in tensile strength in matured rubber is, however, improbable.

3) Dilution of latex gave the following figures (§ 64):

	Tensile strength	Standard time of cure
Crepe from undiluted latex	1.39	110
" " 1 % "	1.37	135

Use of bisulphite (§ 48) gave an increase in tensile strength of 0.0 to 0.05 with a decrease in time of cure of 5 to 15 minutes; formalin (§ 43) gave a decrease in tensile strength of 0.0 to 0.02 with an increase in time of cure of 2 to 5 minutes.

It will be clear that in all such cases the difference in tensile strength may be readily explained by the different time of cure, and that there is no reason to suppose that these chemicals indeed attack the rubber and diminish its real strength.

4) Some cases of large differences in rate of cure may also be quoted. Excess of sulphuric acid gave the following figures (§ 86):

	Tensile strength	Standard time of cure
Normal quantity	1.40	125
Double "	1.36	150
Large excess	1.10	220

The difference in tensile strength between the normal and the double quantity may again be readily explained by the difference in time of cure; but the very low tensile strength when an excess of sulphuric acid was used, is probably due to a real deterioration during vulcanisation by traces of the coagulant.

Alum, when used in large quantities, also greatly retards the rate of cure (§ 88); the following figures may represent the relation between tensile strength and rate of cure:

	Tensile strength	Standard time of cure
Minimum quantity	1.42	125
Double "	1.40	140
Large excess	1.32—1.40	200 — 220

The decrease in tensile strength for the very slow curing samples was in this case much smaller than with sulphuric acid; in some experiments it was even negligible, and it may be regarded as doubtful whether a real deterioration by the coagulant (and not only by the heat) takes place in this case.

Whilst therefore tensile strength and rate of cure, as determined in our method of testing, are not wholly independent, we could as yet not trace any distinct interdependency between *tensile strength* and *slope*, or between *rate of cure* and *slope*.

In the four cases just discussed the slope sometimes increased, sometimes decreased for increasing time of cure, without any regularity. The factors which influence slope enumerated in § 203 sometimes give an increase, but in

other cases a decrease in rate of cure, and in those cases, also, no relationship can be detected. It may, of course, be that the longer heating necessary for slow curing samples indeed does somewhat affect the slope; but the difference, if existing, is so small that we could not yet detect it.

As for tensile strength, it is quite true that inferior samples with a high figure for slope generally show a low tensile strength; and in such cases there may be some common cause which produces inferiority in both properties. But as yet we could not find any relationship or interdependency between tensile strength and slope in this sense that samples with a slope of 34 or 35 show a higher or lower tensile strength than samples with a slope of 38 or 39; or that in cases where the slope increases, the tensile strength invariably decreases. On the contrary, several of the factors enumerated in § 203 (such as prolonged and heavy tapping, and coagulation with alcohol), leave the tensile strength unchanged while increasing the slope. On the other hand, some of the factors which cause a lower tensile strength (such as tapping very young trees, or partial coagulation) seem to be without influence on the slope. It may therefore be assumed that, though a decrease in slope often goes hand in hand with a decrease in tensile strength, and a common cause is then evidently at work, the two properties are in reality independent, as each may be attacked whilst the other is left unaltered.

§ 205. Maximum of tensile strength.

Every type of rubber shows a maximum of tensile strength as described in § 200; its determination may have a certain theoretical interest, but for practical testing it is too laborious, because reliable figures for tensile strength can only be obtained with a large number of rings. Moreover, even if the whole curve of breaking loads has been determined, the exact position of the maximum is not easily ascertained, as in our mixture with $7\frac{1}{2}\%$ sulphur the maximum is rather flat.

We therefore do not determine the maximum tensile strength for every sample, but the tensile strength at a standard state of cure in the neighbourhood of the maximum for ordinary crepe and smoked sheet. The position of the maximum is namely not the same for different samples; it may be found higher or lower on the paper. This is illustrated in Fig. 18 for a sample of first quality crepe, and for a very inferior sample of crepe from washings, which not only shows a low tensile strength but also a maximum which lies much lower on the paper. Comparing, as usual, the length at a load of 1.30 KG for the cures which give maximal tensile strength, we find 990 for sample A, and appr. 910 for the inferior crepe. In the sample of first crepe the tensile strength at standard cure coincides with the maximal tensile strength; in other samples of first grade crepe and sheet the maximum may lay somewhat higher or lower, but the difference between maximum tensile strength and tensile strength at standard cure is never large. In Fig. 14 sample A, for times of cure of 120 and 150 minutes (curves 45 units above and 30 units below the maximum) shows a decrease in tensile strength of 0.03 and 0.04; as an average of a number of samples we found the following figures for curves just above and below the maximum:

Difference in length at 1.30 KG

from curve giving

maximum tensile strength $+20 \quad +10 \quad 0 \quad -10 \quad -20$

Difference with maximal

tensile strength in KG

per mM^2 $-0.02 \quad -0.005 \quad \pm 0 \quad -0.01 \quad -0.03$

The rather flat character of the maximum is evident from these figures, as also from Fig. 14 and 18.

Now the curves giving maximal tensile strength show a length at 1.30 KG of between 970 and 1010 for the great majority of plantation-rubbers. They therefore do seldom differ more than 20 units in length at 1.30 KG from our standard curve; and the difference between our tensile strength at standard cure and the maximal tensile strength is therefore seldom 0.02 or more—which, for ordinary testing, is near or within the error of determination.

In extreme cases, however, the difference is larger; for sample B in Fig. 18 the maximal tensile strength (0.93 KG

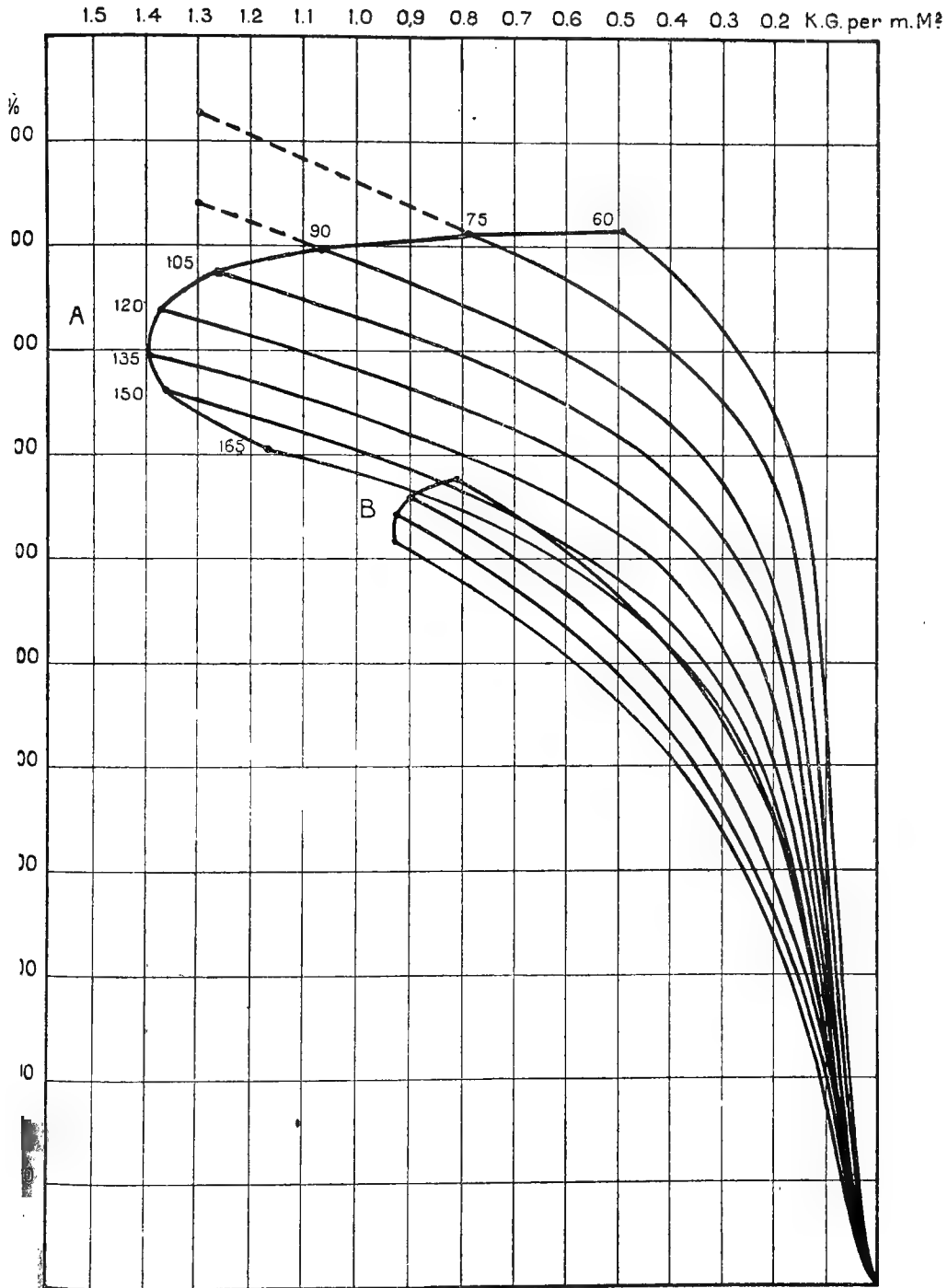


Fig. 18.

Stress-strain curves and breaking points for two samples of rubber;
A first quality crepe, B very inferior crepe.

per mM^2) is appr. 0.10 KG per mM^2 larger than the load found at standard cure. As samples with such an exceptional position of the maximum are always inferior and show a low tensile strength, the accurate determination of tensile strength is mostly of no great practical importance in such cases.

The position of the maximum of tensile strength shows a relationship with slope; the higher the figure for slope (the more inferior the sample), the lower the maximum of tensile strength is found on the paper. Though (as we stated above) it is difficult to determine the position of the maximum exactly in each case, the following figures give a fair average:

Slope	Length at 1.30 KG of curve giving maximal tensile strength
36	992
40	957

whilst a very inferior sample such as B in Fig. 18 with a slope of appr. 53 gives a figure of appr. 910.

Of some importance in comparing testing results is the question whether the curves for breaking loads intersect or not; or, in other words, whether a low figure for tensile strength found at a certain state of cure means a low figure for all cures.

Now there is no doubt that curves such as for sample A and B in Fig. 18 do intersect, or at least would intersect if curve A could be prolonged in the over-vulcanised state so far as to reach curve B. In other cases also, where the position of the maximum is different, the curves must intersect; but for samples with the same slope, giving maximal tensile strength on the same stress-strain curve, the curves for breaking loads seem to run parallel, or at least form congruent figures. An example is given in Fig. 19, where V represents the curve of breaking loads for rubber from the first clot obtained in partial coagulation (see § 176),

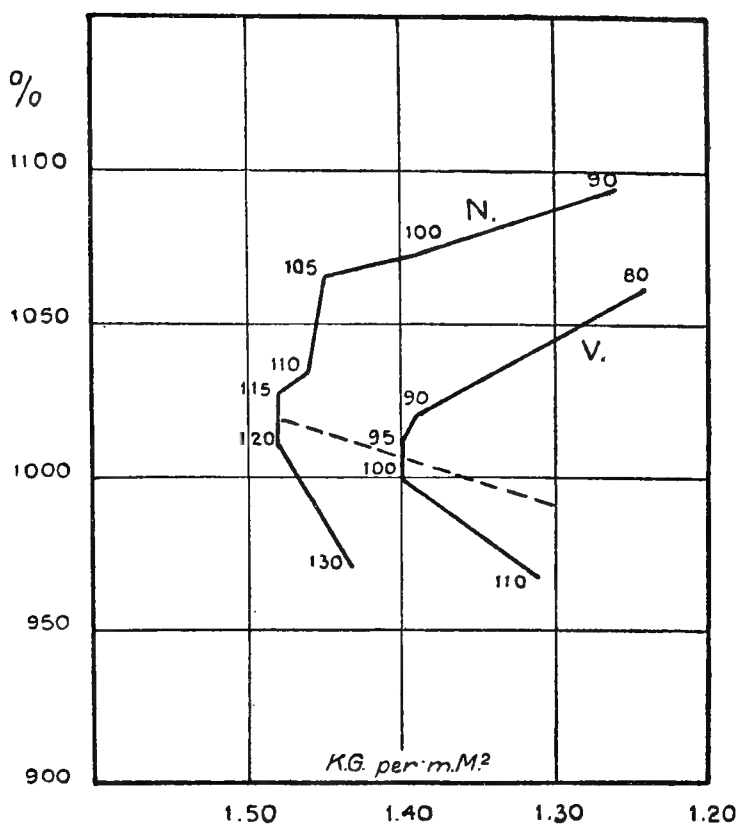


Fig. 19.

Breaking points for increasing times of cure. Sample V pre-coagulation; sample N crepe from the rest of the same latex. Dotted line: position of our standard curve.

and N the breaking loads of the rubber from the rest of the latex. It will be seen that the first clot shows a lower tensile strength on every stress-strain curve.

Further illustrations of curves of breaking loads with the maximum in the same or in other position, see O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 773; J. S. Ch. I. 38 (1919), 92 T; I. R. J. 57 (1919), 1164.

§ 206. Coefficient of vulcanisation.

In § 200 we described how during vulcanisation a reaction takes place between rubber and sulphur, during which the sulphur enters into what is called the „combined” state.

While sulphur is readily soluble in acetone and easily extracted by it from a rubber-sulphur mixture, the „combined” sulphur is not soluble and from a vulcanised rubber only the free sulphur is extracted with acetone; the combined sulphur can be determined in the rubber after extraction. The amount of combined sulphur calculated as percentage of the rubber is called the coefficient of vulcanisation.

Whether the combination between rubber and sulphur constitutes a mere chemical reaction in the strict sense of the word, or whether physical changes also play a role, still forms a point of discussion which we leave out of consideration. The fact which here interests us is that the combined sulphur shows the characteristics of a chemical combination in so far that it is constant under circumstances in which the physical properties of rubber, and amongst them what are generally called the mechanical properties, change in the manner well-known for colloids. Simply storing the sample may be named as one of the most important factors which change the physical or mechanical properties, but leave the „combined” sulphur unchanged; the temperature at which the vulcanisate is tested, is probably another one.

For keeping at ordinary or elevated temperature this is not strictly correct; samples with a low coefficient of vulcanisation show no or only a small increase at temperatures below 70° C, but in longer cured samples there may be a decided increase (see § 209).

This makes the coefficient of vulcanisation a better gauge on the state of cure than the mechanical properties, especially when comparing tests effected under different circumstances; probably the coefficient of vulcanisation is the best scientific base for comparison in such cases. When, however, the conditions of curing and testing have been rigidly fixed and remain the same throughout, there is a very close relationship between mechanical properties and coefficient of vulcanisation. The combination between rubber and sulphur proceeds slowly during vulcanisation, and in direct proportion to the time of cure. For our method of testing some examples are given in Fig. 20, in which the coefficient of vulcanisation is plotted against time of cure. Sample 42 Z is the quickest curing, No. 491 has the smallest rate of cure, but in all

cases the coefficients for successive cures lie nearly on a straight line, at least as long as not more than 5 parts of sulphur have gone into combination. When curing further, only a small quantity of free sulphur is left, and the reaction goes slower and slower, the lines in Fig. 20 become less

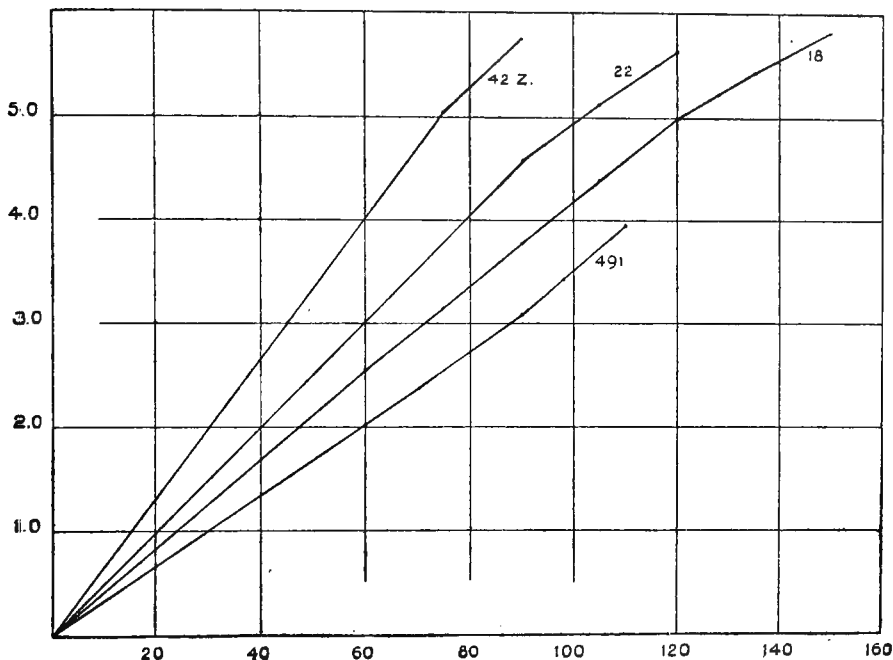


Fig. 20.

Coefficient of vulcanisation at different times of cure for samples with different rates of cure.

steep and finally tend to take a horizontal course. For coefficients of vulcanisation below 5 there is a direct ratio between time of cure and coefficient; the factor or ratio however differs according as the sample cures faster or slower.

See similar results by D. SPENCE and J. YOUNG (Z. Koll. 11 (1912), 33), D. SPENCE and C. A. WARD (Z. Koll. 11 (1912), 297), K. GOTTLÖB (G. Ztg. 30 (1916), 304 and 326), F. C. VAN HEURN (Comm. Delft VI, page 183 and 186), H. P. STEVENS (J. S. Ch. I. 37 (1918), 284 T), and others.

G. D. KRATZ and A. H. FLOWER (I. R. W. 59 (1919), 194) for a mixture containing zinc oxyde, an accelerator and 5% rubber on the sulphur, found the graph to take a curved form when about 3 parts of sulphur had entered into combination.

They obtained a straight line by applying a „rising cure”, starting at 285°⁵ F and finishing at 307°⁰ F.

For the rate of combination when higher percentages of sulphur are taken see H. SKELLON (Z. Koll. 14 (1914), 103, further Rubb. Ind. 1914, page 172) and G. VAN ITERSOM (Comm. Delft VII, page 245).

As the mechanical properties also change in a regular manner with increasing time of cure, a similar relation between coefficient of vulcanisation and mechanical properties may be expected. In fact, for different samples the coefficients of vulcanisation for a fixed stress-strain curve show only small variations. The average figures for our method of testing are:

Position of stress-strain curve (length at 1.30 KG)	Average coefficient of vulcanisation
1050 %	4.2 ⁵
1030 „	4.5
1010 „	4.7 ⁵
990 „	5.0
970 „	5.2 ⁵
950 „	5.4 ⁵

The increase or decrease in coefficient of vulcanisation for 1 unit difference in length at 1.30 KG is 0.013 in the neighbourhood of our standard state of cure.

The values actually found for different samples may differ somewhat from the average, but the deviations are seldom larger than 0.5, so that the coefficient of vulcanisation for our standard cure in nearly all cases lies between 4.5 and 5.5, and mostly close to 5.0.

A. VAN ROSSEM (Comm. Delft V, page 164) calculated the position of the stress-strain curves for fixed coefficients of vulcanisation, and found a variation (probable deviation from the average) of 8.7 KG per cm² at 850 % extension; so that 50 % of all curves show at 850 % elongation a load which deviates not more than 0.09 KG per mm² from the average. This means a deviation in coefficient of vulcanisation for a fixed curve of ± 0.35 .

Though the coefficient for a fixed curve (for instance our standard curve) therefore shows small, though distinct variations, it has not yet been possible to connect these deviations with any property of the rubber, in such a manner that for instance a coefficient higher than the average would be an indication of certain mechanical properties or of a certain special composition of the rubber. Perhaps these deviations from the average coefficient may in future gain some importance and be found an indication of some hitherto overlooked property of the rubber; but at the present nothing is gained by determining the coefficient *besides* the stress-strain curve, as long as the testing goes along one rigidly standardised line.

As the determination of the coefficient of vulcanisation means a considerable amount of additional work, and gives no actual gain in the routine of our testing of estate-samples, we have not included it in our regular tests. We use the coefficient of vulcanisation only when testing samples of a special composition, or in the study and comparison of methods of testing.

§ 207. Permanent set.

A property which is often determined in rubber testing is the set or deformation in some form or other. We have for some time regularly determined the permanent set, in the form of the elongation after stretching rings to five times their original length during 24 hours, and measuring the length 6 hours after releasing.

On the method of determining permanent set see § 222.

Permanent set, like tensile strength, changes with the state of cure and decreases, the longer the sample is cured. For too long cured samples the determination of this property becomes difficult or impossible, as overcured rings do not stand the stretching and break during the pulling of them onto the glass plate, or during the period they are stretched.

As an average we found the following figures for the difference in permanent set with increased time of cure (state of cure expressed, as usual, by the position of the stress-strain curve).

State of cure (length at 1.30 KG)	Permanent set
1040	+ 0.65
1030	+ 0.48
1020	+ 0.33
1010	+ 0.20
1000	+ 0.09
990	± 0
980	— 0.07

See O. DE VRIES and H. J. HELLENDORF, J. S. Ch. I. 36 (1917), 1260. Further figures for the decrease in deformation with increasing times of cure see for instance P. BREUIL, C. Gp. 1911, page 5298.

To compare the permanent set of different samples it is necessary to bring them to a comparable state of cure, for which we, of course, chose our standard cure. The permanent set at standard cure for ordinary samples of crepe or sheet shows figures between 2 and 3¹/₂, but for the lower grades much higher figures may be found, amounting even to 10 or 15.

See O. DE VRIES and H. J. HELLENDORF, l.c. page 1259 and 1261.

In comparing these figures with the other properties of the rubber, a very close relationship between permanent set at standard state of cure and slope came to light. In the average the figures are:

Slope	Permanent set at standard state of cure
34	1.9
35	2.2
36	2.53
37	2.87
38	3.2
39	3.54
40	3.9
41	4.3
42	4.75

From these average figures the actual permanent set may deviate 0.1 to 0.2 units, which is very near the limit of error in determination.

In some special types of rubber abnormal figures were found. In how far this may form an indication as to special properties of these rubbers, and in how far figures for permanent set not showing the normal relation to slope may in future become important in testing, has not yet been further investigated.

See O. DE VRIES and H. J. HELLENDORF, *l. c.* page 1261.

The relation between slope and permanent set has not yet been worked out further. Probably a deeper study of the mathematical and physical side of this relationship would throw considerable light upon the relations between the structure and the mechanical properties of vulcanised rubber.

As, in ordinary testing, the relationship between slope and permanent set is so close as to lie within the errors of determination, permanent set tests may be dropped out from the ordinary routine testing. Permanent set tests require additional rings, whilst slope is determined from the same curve as tensile strength. The deviations in permanent set for special types of rubber, mentioned above, deserve further investigation.

§ 208. Other properties.

A large number of instruments and machines have been invented to test vulcanised rubber on properties other than those treated in the foregoing paragraphs. We may mention hysteresis, abrasion, hardness, resiliency, rebound, torsion, compression and a number of others. Practical tests, in which the article in its final form is subjected to a treatment similar to, but much more intensified than, it will have to stand in actual use, may also be of great importance in testing rubber articles.

Though such tests deserve full attention, they do not enter into the plan of this book, as they are in the first place destined to judge the technical mixture and the manner

of vulcanisation. Any relationship between such tests and the properties of the raw rubber itself has not yet been developed, and probably the properties of the raw rubber do only for a very small part influence the results, the treatment in manufacture being far more decisive.

Rubber being a substance which derives its eminent technical importance from its special physical properties, the investigation of its physical constants and properties under different circumstances would seem of the utmost importance. Still the knowledge of the relationship between technical requirements and the physical properties of vulcanised rubber objects is very little developed, and still less is known of the relationship between rubber-preparation on estates and the various properties of the vulcanised product. For judging and comparing the properties of raw rubber tests such as those mentioned above are, up to the present, without importance. It is to be hoped that certain relationships may be worked out in the future, so that new tests of raw rubber can be developed. Up till now, however, there is no indication as to in which way such tests can give results that may not be obtained more easily and in a more clearly defined form by the simple tests described in this chapter.

Especially the slope and form of the stress-strain curve seem destined to give valuable indications regarding different properties, as they do in the case of permanent set.

§ 209. Ageing tests.

Whilst, as treated in Chapter XII, raw rubber is a relatively stable product, and may be kept for many years without appreciably changing its properties, the vulcanised product behaves differently. From the moment vulcanisation is finished or better broken off, changes continue to go on slowly which may adequately be termed after-vulcanisation, and which finally, be it after a shorter or a longer period, lead every vulcanised article to complete deterioration. There is a rather striking contrast between the stability against outer influences (heat, sunlight, chemicals and so on) — which is much greater in vulcanised than in raw rubber, and makes vulcanisation such a valuable process—and the stability

on ageing, in which vulcanised rubber is much inferior to the raw product.

The greater stability of raw rubber, as compared with the vulcanised product, was clearly pointed out by H. P. STEVENS (J. S. Ch. I. 37 (1918), 341 T).

It is known to every one that vulcanised rubber, as time goes on, becomes hard and brittle, and finally perishes. About the exact nature of these changes, the laws they follow and the factors by which they are influenced, very little exact data are available; though in this, as in many other cases, the matter collected and kept shut up in a most inefficient manner by a number of manufacturers is probably very large.

On an accelerated ageing-test in hot air see W. C. GEER, I. R. W. 55 (1916), 127.

We here only discuss the changes on ageing of vulcanised rubber-sulphur mixtures treated in our usual manner.

The coefficient of vulcanisation, as we mentioned in § 206, remains unaltered or increases only a little, when keeping vulcanised slabs at ordinary temperature; when the coefficient of vulcanisation is high, the increase on keeping may be larger:

H. P. STEVENS, J. S. Ch. I. 37 (1918), 305 and 340; B. J. EATON and F. W. F. DAY, J. S. Ch. I. 38 (1919), 345 T.

When calculating the increase in combined sulphur in such cases it is necessary to reckon with the increase in weight by oxydation under formation of sulphuric acid, which takes place in vulcanised rubber on keeping (see below).

The Government Institute at Delft (Comm. Delft VI, page 219) found an increase in coefficient of vulcanisation of 0.0 to 0.28 on keeping for one year; the increase for samples with high coefficients was not found larger than for shorter cured vulcanisates.

This holds for temperatures up to 70 or 80° C. At higher temperatures the coefficient slowly increases on keeping the vulcanisate, the change becoming quicker as the vulcanising temperatures are approached.

See D. SPENCE, Z. Koll. 10 (1912), 299.

D. F. TWISS and S. A. BRAZIER (J. S. Ch. I. 39 (1920), 129 T) found that the temperature-coefficient of the reaction between rubber and sulphur remains constant (about 2.5 for 10 degrees Celsius) from the ordinary vulcanisation-temperatures down to 108°; between 98 and 108° the coefficient shows a value of more than 5, and below 100° the velocity of this reaction probably decreases rapidly, to become negligible for temperatures below 70°.

The chemical composition of vulcanised mixtures of rubber and sulphur shows marked changes. The total weight increases by oxydation; the increase is small for ordinarily cured samples, but may reach values such as 25 and even 40 % in nine months for over-cured samples. Sulphuric acid is formed, whilst the watery and the acetone-extract show an increase and may amount to 25 % and higher.

About the formation of acid on keeping see K. BING (Z. Koll. 4 (1909), 232; also I. R. J. 37 (1909), 685) who observed the presence of sulphuric acid and found it to accompany the changes (getting hard and brittle, or tacky) in the vulcanised product.

H. L. TERRY (J. S. Ch. I. 31 (1912), 1104) also studied the formation of acids on keeping vulcanised rubber.

B. J. EATON and F. W. F. DAY (J. S. Ch. I. 38 (1919), 345 T) studied these changes more extensively and found remarkable increases in weight, and in acetone or water soluble parts, which well deserve further attention.

The physical and mechanical properties also change. For three slabs of the same sample, brought to different states of cure, these changes are illustrated by Fig. 21. They consist of the following:

- 1) the stress-strain curve gradually comes lower down on the paper, that is the elongation produced by a certain load, after storing, becomes smaller; the vulcanisate, on keeping, becomes harder or stiffer.

This downward movement of the stress-strain curve is nearly the same for all states of cure, from the ordinary technical cure A with a coefficient of vulcanisation of appr. 3, to the cure giving maximal tensile strength C, with a coefficient of nearly 5. Only in the initial stage is the downward movement somewhat quicker for shorter cured samples.

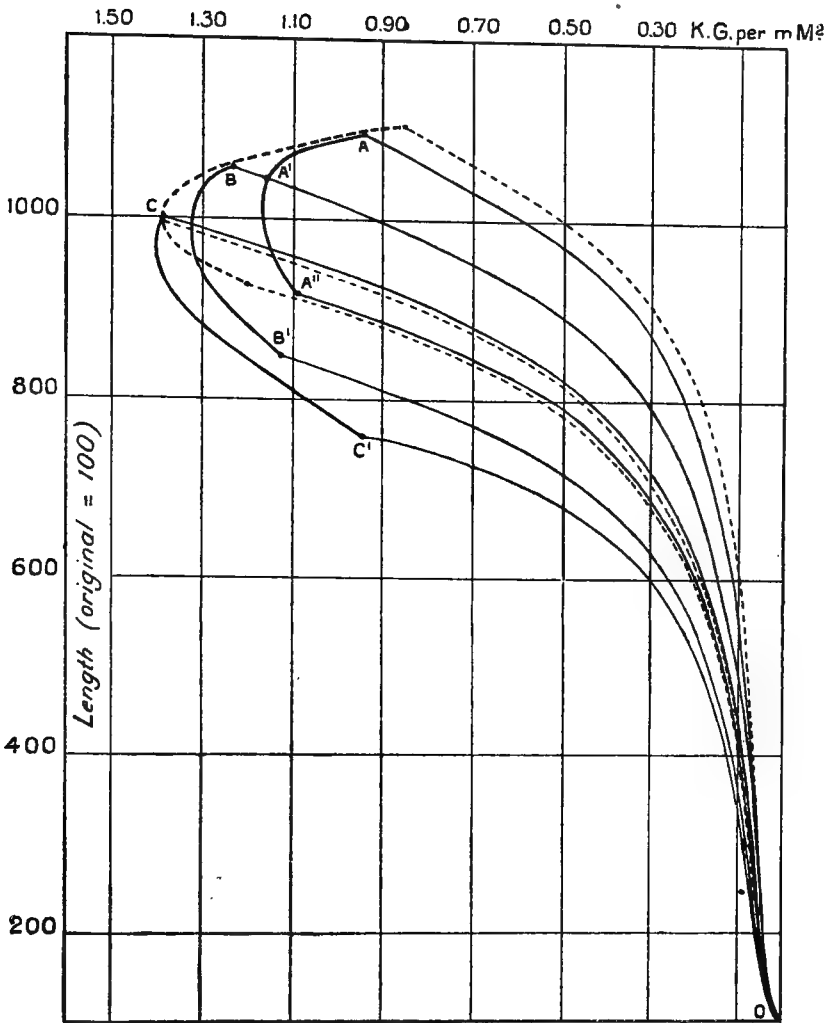


Fig. 21.

Changes in mechanical properties in vulcanised rubber on keeping.
 Dotted lines: stress-strain curves and curve of breaking points for ordinary vulcanisation, as in Fig. 14 and 18.
 Continuous lines: stress-strain curves and curves of breaking points on ageing.

The downward movement becomes slower and slower, the longer the sample is kept. Whilst, in our testing, during the first week the decrease in length for a certain load per day may be 0.5 units on a total length

of 1000—1100, it gradually becomes smaller, without however coming to a complete stop, at least in vulcanised slabs kept for 2—3 years.

- 2) The tensile strength at first increases in the same manner as it increases in prolonged vulcanisation; but gradually the tensile strength of the aged sample lags behind, and for a certain curve OA' the tensile strength on ageing (A') is much smaller than would be found if the same stress-strain curve had been reached by continued vulcanisation (B).

The tensile strength, after some time, reaches a maximum and then diminishes, so that finally the vulcanisate becomes brittle and loses its strength.

In general character these changes are the same for different states of cure; but the practical effect is not the same, as the longer cured samples such as B and C reach the maximum of tensile strength and the state of brittleness in a shorter time than samples such as A.

See O. DE VRIES and H. J. HELLENDORF, Arch. 4, Nov. 1920. For similar changes at temperatures of 60—70° see O. DE VRIES, Arch. 2 (1918), 802.

H. P. STEVENS (J. S. Ch. I. 37 (1918), 305 and 340 T), using a mixture of 90 rubber and 10 sulphur, and keeping it at the varying and sometimes low European temperatures, found substantially the same changes, though in detail there are interesting differences, well worth further investigation.

J. BOUTARIC (C. Gp. 1911, page 4966) on keeping vulcanisates at 45° C found the properties to pass through a maximum and then decrease more or less rapidly. He recommends a temperature of 18° for storing the rubber, eventually by the use of artificial refrigeration.

Having thus fixed some of the changes in vulcanised rubber-sulphur mixtures at ordinary room-temperature (27° C) in our method of testing, the principal question which interests us in this book is: how are these ageing phenomena influenced by differences in latex and preparation?

The influence of such factors was found to be smaller than is generally expected. There is a, probably quite warranted, fear of deterioration on ageing of vulcanised articles; but it would seem that the blame has many times

quite unjustly been thrown on the raw rubber. Mistakes in manufacture, inexactness in curing, unsuitable mixtures would probably have given the explanation, had the causes been investigated thoroughly.

Of course, differences in rate of cure in plantation-rubber may cause trouble in this respect, and are quite justly protested against; but when these differences are taken into account, and the rubber brought to the correct state of cure, it would seem that differences in method of preparation, at least those actually occurring in estate-practice, are wholly without influence on the ageing properties of the rubber.

We found to be without influence on the ageing in the above described sense:

- 1) coagulation with different doses of acetic acid, ranging from $\frac{1}{2}$ to 2 cc per liter of latex, that is a wider range than actually occurs in estate-practice (see § 83).
- 2) the use of sulphuric acid in small doses ($\frac{1}{4}$ to 1 cc per liter of latex), as compared with acetic acid (see § 86).
- 3) coagulation with sodium chloride (10 gms per liter of undiluted latex). See § 90.
- 4) coagulation with sugar (see § 96).
- 5) rolling a different number of times, from 3 to 24, in the preparation of crepe (see § 118).

Even the last factor — which is so often supposed to have a harmful effect on the rubber by those who confound the rolling of dry, several months old rubber (after arrival in Europe or America), with the milling of fresh, wet coagulum — was found without influence on the changes in vulcanised samples on keeping.

Special methods of preparation may, however, produce somewhat different ageing properties. Matured rubber (§ 108), balls prepared after the Brazilian method (§ 187), or rubber from dried up latex (§ 193) show a somewhat more rapid downward movement of the stress-strain curve (the vulcanisate sooner becoming stiff); in the lower grades this change may be still more rapid (2—3.5 units in length per day, against 0.5 for first quality).

In other cases, such as pre-coagulation (§ 176) or very inferior crepe from washings (§ 179), the falling off in tensile strength was much more rapid than in the ordinary types.

As a whole, however, the changes on ageing of vulcanised slabs, tested in the above described manner, are very similar for samples of different origin and for the usual differences in methods of preparation; and the ageing properties, up till now, did not give much indications as to the best or a better method of preparation. This is, perhaps, contrary to what many would have expected. It may be that tests can be developed on other properties which on ageing are more influenced by the method of preparation; but the fear of the influence of the composition of the latex and the methods of preparation on the ageing of vulcanised rubber seems to be much exaggerated.

For changes in mechanical properties on keeping in mixtures of other composition see, for instance, J. BOUTARIC, C. Gp. 1911, page 4966; CL. BEADLE and H. P. STEVENS, I. R. J. 52 (1916), 401 and 679; PH. SCHIDROWITZ and H. A. GOLDSBROUGH, I. R. J. 52 (1916), 617.

CHAPTER XVIII.

VULCANISATION-TESTING.

II. Details of our method of testing.

After having described in the foregoing chapter the general course of our method of vulcanisation-testing we will now treat some of the technical details and discuss the sources of errors and deviations so far as we have investigated them.

§ 210. Rubber and sulphur.

Rubber.

The rubber, in our testing, is always used in the air-dry state. This means a moisture-content of 0.3 — 1 % for ordinary crepe or smoked sheet (see § 241); the ratio of sulphur to (dry) rubber in the mix from 8.108 changes at the most to 8.19 from this factor. As the time of cure diminishes by 2½ minutes for an increase in sulphur-content of the mixture of 0.1 unit (compare § 223), the above maximal difference only means 2 minutes in time of cure, so that the small differences in moisture-content of the rubber from day to day, or from the cool morning hours to the heat of midday — which will seldom reach 0.5 %, corresponding with 1 minute in time of cure — for practical purposes do not count as a source of variation in the figures for rate of cure.

We made some special experiments by keeping weighed portions of the same sample of rubber some days in a moist and in a dry atmosphere before the sulphur was mixed in. The results after vulcanisation were identical; the moisture seems wholly to be evaporated during plasticising and mixing.

Samples of crepe and smoked sheet are tested in the form in which they reach us from the estates, without

washing and recrepeing. Lower grades are also mostly tested without preliminary washing; in some cases (see for instance the example in § 177) recrepeing is necessary.

The washing and remilling of ordinary crepe and smoked sheet is wholly without influence on the results obtained in testing.

See B. J. EATON, Agric. Bull. F. M. S. 3 (1915), 190 and Bull. F. M. S. No. 27 (1918), 306. Further Bull. Ceyl. No. 23 (1915), 5 and Bull. Imp. Inst. 16 (1918), 447. Our own rather large experimental material on this point wholly confirms the above conclusions; only by excessive washing and crepeing of matured rubber did we find a small decrease in rate of cure, evidently caused by the washing out of some accelerator.

Smoked balls prepared after the Brazilian method and also other types of rubber that contain a rather large amount of moisture, such as slab-rubber (§ 192), have either to be cut into pieces and dried, or to be creped and dried before vulcanisation. It is remarkable that ordinary washing and crepeing does not cause a change in rate of cure in such types of rubber: the substances that are most easily washed out seem without influence on rate of cure, while the accelerators of vulcanisation seem to be absorbed rather strongly.

Smoked balls prepared after the Brazilian method show the same rate of cure when completely air-dried as after washing and crepeing; the tensile strength however was often found to improve by crepeing, evidently from the washing out of pieces of dirt.

Similarly rubber obtained by evaporation, which contains all serum-substances and loses a considerable part of them in washing and crepeing only shows a small increase in time of cure (say 5 minutes) after washing and crepeing (compare § 102).

G. S. WHITBY (J. S. Ch. I. 35 (1916), 498; also I. R. J. 51 (1916), 793) found tensile strength, rate of cure and slope the same in recropped pieces of ball-rubber as in pieces simply dried in a desiccator.

Sulphur.

The sulphur is strained through a wire gauze sieve with 30 holes per cm; it is used in the air-dry state. The

moisture-content of the air-dry sulphur is seldom higher than 0.05 %, and generally only 0.01 or 0.02 %, so that it does not influence the results.

It is well known that what is sold under the name of flowers of sulphur, sublimed sulphur etc. is a very variable product. The solubility in carbon bisulphide varies largely, the melting point ranges from 110—120°, and the degree of fineness also shows large variations. Rather coarsely powdered molten sulphur, real sublimed sulphur and amorphous sulphur may all be found in the commercial product.

The different forms of sulphur obtained in commercial sublimation and their solubility in carbon bisulphide are described by G. NOYER (C. Gp. 1918, page 9661). See further on the commercial types of sulphur, their preparation, composition and analysis, P. BREUIL, C. Gp. 1909, pages 3336 and 3436, *ibid.* 1910, pages 3604 and 3707.

D. F. TWISS (J. S. Ch. I. 36 (1917), 787; see further Ann. Rep. Soc. Chem. Ind. 4 (1919), 327) compared crystalline and insoluble sulphur and found no appreciable difference in vulcanisation.

For theoretical considerations of the possible influence of the different modifications of sulphur see for instance D. F. TWISS, *l. c.*; G. VAN ITERSSEN, Comm. Delft VII, page 253.

In testing a number of samples of sulphur from different sources we found that the type of sulphur may have rather a large influence on the vulcanisation-results. Apart from cases in which the tensile strength of the rubber is found low, probably because of particles of dirt, a difference in length at 1.30 KG of 40—50 units and more is often found for samples of rubber cured side by side but with sulphur from different origin, corresponding with a difference of 10—15 minutes in standard time of cure. It is therefore necessary to use one large homogeneous stock of sulphur, and to check new supplies so that deviations from this cause are avoided. The deviations in rate of cure of the rubber-sulphur mixture are probably caused by impurities in the sulphur; no details as to their nature are as yet known.

§ 211. Mixing.

The manner in which the rubber is rolled and mixed with the sulphur is described in § 198. At first we adopted

very rigidly standardised methods of rolling during this mixing process; numerous experiments however made it clear that practically no differences are caused by small alterations in the process, provided the temperature during mixing is kept within fixed limits. As an example we may mention the following figures for mixtures prepared without any special care from the same sample of rubber by three operators, and vulcanised side by side.

Operator	Tensile strength	Length at breaking	Length at 1.30 KG	
A	1.29	1004	1005	
B	1.29	1004	1005	
C	1.33	1010	1003	

In the same way, mixtures prepared by the same operator on one day or on different days, and vulcanised side by side, seldom show larger deviations than 0.05 in tensile strength and 10 units in length at 1.30 KG, that is the ordinary error of determination if a small number of rings is tested. In a large series of control tests, in which three separate mixtures from each sample of rubber were vulcanised side by side, and 5 rings tested of each mixture, the average deviation from the average tensile strength was 0.022, and from the average length at 1.30 KG 2.1 units.

Extra milling after the rubber-sulphur dough has become sufficiently homogeneous and plastic gives no difference in the properties after vulcanisation. In some of the experiments we even found a slight increase in tensile strength for an extra milling of 17 times. Of course these data hold only for the conditions under which we work: relatively small batches of rubber and sulphur mixed on small experimental mills; under these conditions extra milling does not seem to be a source of errors or deviations in the results.

The temperature during the mixing operation is not controlled by thermometer, but only by hand. As the mixing takes

place at temperatures at which the hand is very sensitive, this way of controlling is quite satisfactory. Thermometer-determinations must be made by enveloping the thermometer in the mixture to obtain the exact temperature of the mixture itself. From time to time we control the process in this way, but in daily practice a control by the trained hand is quite sufficient.

The temperature reached during the mixing process has a considerable influence on the results. Too low temperatures cause a deficiency in tensile strength, whilst high temperatures result in a somewhat more advanced cure. As an example we may mention the following typical figures for different mixes from the same sample of rubber:

Temperature of rolls	Final temperature of mixture	Times rolled	Tensile strength	Length at breaking	Length at 1.30 KG
40 — 48	46	31	1.19	978	996
48 — 56	50	28	1.24	980	989
50 — 63	54	25	1.34	990	984

Though these differences in temperature, expressed in figures, may not seem large, they are conspicuous enough in actual mixing. The first sample was kept too cold, mixing was rather difficult; it had to be rolled 31 times, instead of our usual 22—25 times, to get it sufficiently plastic for the calender. When higher temperatures are used, the mixing is easier.

The increase in tensile strength, by mixing hotter, is very striking and was found to recur in all the experiments in question. The differences in length at 1.30 KG only range over some 10—15 units, that is somewhat less than 5 minutes in time of cure.

The temperature reached during the mixing operation should therefore be well controlled; in cases in which a low tensile strength is found, a repeat test may be desirable to check whether the mixing was not done at too low a temperature. Luckily when once the hand of the operator is trained and hardened, the inclination is to increase the

temperature rather than to keep the rolls cold, so that the danger for too low figures for tensile strength from mixing at too low a temperature is in practice not large. Nevertheless this point deserves attention and adequate supervision.

An upper limit of temperature is formed by the mixture becoming somewhat sticky, so that in calendering it sticks to the cloth and is not easily removed from it.

CL. BEADLE and H. P. STEVENS (J. S. Ch. I. 30 (1911), 1425; also I. R. J. 43 (1912), 48, and *ibid.* 46 (1913), 164) found that additional mastication, after mixing a compound in the usual way, gave an increase in set (deformation) after stretching with a given load. The effect was greatest on pale crepe, least on smoked sheet, while fine hard Para took an intermediate position.

J. BOUTARIC (C. Gp. 1911, page 4965) found prolonged masticating (kneading on hot rolls before the sulphur is mixed in) to give a marked decrease in tensile strength in first grade American rubber, and a very marked decrease in low grade African rubber.

D. SPENCE and C. A. WARD (Z. Koll. 11 (1912), 277) found mastication during 90 minutes on very hot rolls (after which sulphur was mixed in in 10 minutes) to give a markedly smaller tensile strength than masticating during 30 minutes on moderately heated rolls. The coefficient of vulcanisation (rate of cure) was, however, not in the least affected by this drastic treatment.

G. BERNSTEIN (Z. Koll. 12 (1913), 274) holds the mechanical treatment, combined with heating to 80°, to be the cause of incipient vulcanisation in quick-curing mixtures, which do not show this incipient vulcanisation when simply heated to the same temperature. The explanation is a depolymerisation which, according to this author, must precede vulcanisation.

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 58 (1919), 617) studied the effect both of grossly over-masticating the rubber before mixing in the sulphur, and of mixing for a period much longer than the normal. Over-mastication was found to retard the rate of cure, and prolonged mixing (probably due to incipient vulcanisation) to shorten the curing period.

The same authors (J. S. Ch. I. 38 (1919), 350 T) found mixing in the laboratory to give the same tensile strength and slope and approximately the same time of cure as mixing on a works machine.

P. DEKKER (Comm. Delft VI, 182) found extra plasticising up to 60 times without influence on the coefficient of vulcanisation, though the viscosity of the rubber-sulphur mixture decreased to nearly $\frac{1}{3}$ its original value.

F. C. VAN HEURN (Comm. Delft VI, page 205) found plasticising for 10 or 30 minutes of no great influence on the mechanical properties of the vulcanisate. Prolonged energetic plasticising was, however, found by A. VAN ROSSEM (ibid. page 205) to decrease the tensile strength.

D. F. TWISS and S. A. BRAZIER (J. S. Ch. I. 39 (1920), 125 T) mention that mastication and mixing have a tendency to increase the extensibility (elongation produced by a certain load).

E. SEIDL (G. Ztg. 34 (1920), 797) concludes that mastication gives a decrease in strength and resistance to stretching, but leaves the rate of combination with sulphur unaltered.

The influence of kneading on hot rolls and of similar operations on viscosity are treated in § 236.

§ 212. Calendering.

To the casual onlooker the calendering of the mixture of rubber and sulphur seems the most simple of all the operations to which the rubber is subjected during testing. In reality it requires special care to regulate the temperature of the calender-rolls, their distance and speed, so that an even sheet of appr. 2 mM is always obtained. Rather strict standardisation is necessary to obtain regularly a good sheet of even thickness that does not stick to the cloth.

Three layers of this sheet are pressed one on the top of the other by a small rolling pin in the usual manner; this gives the final slab, from which pieces of a certain weight (see § 199) are cut to be put into the steel frames for vulcanisation.

The thickness of this final slab seems to be of some importance for the results; too thin slabs, of 4 mM instead of somewhat more than 5, gave a product in which vulcanisation was more advanced (15—20 units in length at 1.30 KG, or appr. 5 minutes in time of cure) than in control slabs of the ordinary thickness (see also § 213).

The fresh slab is dusted with talc-powder to prevent it from sticking. Some talcum may, of course, be incorporated in the vulcanised rubber, and the influence of it has therefore to be ascertained.

In comparing a number of samples of talcum of different origin we found no difference in tensile strength or rate of cure of the rubber, so that the use of this substance does not cause errors or deviations in the results.

The addition of 1 or 2 % of talcum to the ordinary rubber-sulphur mixture left tensile strength, rate of cure and slope absolutely unchanged, so that even unusually large quantities of talcum, if incorporated into the vulcanised slabs by some accident, are without influence on the testing results.

CL. BEADLE and H. P. STEVENS (J. S. Ch. I. 30 (1911), 1421) found the addition of $\frac{1}{2}$ and 2 % of talc to a mixture of 5 sulphur and 100 rubber to cause a slight increase in coefficient of vulcanisation and also a slight increase in the deformation after stretching to a certain load.

§ 213. Keeping the mixture.

In our method of testing each sample of rubber is vulcanised two or more times: first in a trial vulcanisation, then in a final vulcanisation, which latter is repeated if the result needs corroboration. For these different vulcanisations, which may take place at intervals of several days, we generally use parts of one and the same mixture; the time between mixing and vulcanisation is therefore not kept constant. Of course the rule might as well be followed of making a fresh mixture for every vulcanisation, by mixing on one day all the slabs to be vulcanised on the next day. This however means additional work, whilst keeping the mixture for some days or even weeks is not, as far as we could ascertain, a source of error.

The effect of keeping the mixture before vulcanisation is best tested by mixing portions of one sample at different times, and vulcanising them side by side in one charge, so that no differences can be caused by the temperature and other conditions of vulcanisation. Even in extreme cases of mixtures kept for several months we found the tensile strength the same as for fresh mixtures, while the length at 1.30 KG sometimes showed differences varying from 5 to 15 units, the old mixture showing a smaller time of cure, so that perhaps during long storing pre-vulcanisation may have taken place to a small degree.

The effect of keeping the mixtures in actual factory-practice may, of course, be quite otherwise, as they may have undergone a much more drastic treatment and contain, besides rubber and sulphur, a number of other substances. D. SPENCE and C. A. WARD (Z. Koll. 11 (1912), 276) regard it as a generally acknowledged fact that mixings which have been stored for some weeks show appreciable changes in properties after vulcanisation.

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 58 (1919), 617), working with a mixture of 100 rubber and 8 sulphur, found that differences in the time between mixing and curing of from 1 to 7 days gave no appreciable differences in the testing results after vulcanisation, and that for practical testing they are not of serious importance.

Our mixtures are kept in subdued light in a cupboard; we have not yet investigated whether our rubber-sulphur mixture is sensible to strong daylight or direct sunlight.

On the effect of light on unvulcanised mixtures containing other compounds, see R. REPONY (Rubber Age & Tire News 5 (1919), 191; also I. R. J. 58 (1919), 72). REPONY found light, and especially direct sunlight, to have a strong effect on some mixtures, containing a high percentage of mineral filler.

§ 214. Vulcanisation.

In § 199 we have already described the general course of vulcanisation and the rules followed in the accompanying operations. Some further details may be mentioned here.

The slabs of rubber-sulphur mixture are purposely made somewhat thicker than the steel frames which determine the final thickness of the vulcanised slabs (6 mm as compared with 5), so that the weighed pieces of mixture fit easily in the frames. Very soon in the beginning of the operation (partly already in the pile that is waiting to be put into the pan as soon as the foregoing vulcanisation is finished) the dough, weaker as it gets warm, is pressed together to the thickness of the frames, fills the space in the frame and exudes through the openings left in the frame for this purpose. We have repeatedly investigated whether any unevenness in properties arises from this movement of the dough, eventually near the openings (by putting marks on the rings before they are punched) but could never find that the rings break in any one place earlier than another.

Too thick slabs (7 mm and more) do not cause trouble and are distributed evenly in the frame as they become hot; too thin slabs, which are longer or broader than the frame, may give deviating results. In § 212 we mentioned that such slabs give a somewhat more advanced curve (apparently cure quicker). The exact explanation is not yet known; it may be that the thinner slabs are sooner warmed to the interior, or that thin pieces or films of rubber-sulphur mixture are pressed between frame and plate and allow an easier access of steam and heat to the contents of the frame.

As mentioned in § 199 we weigh a portion of mixture for each slab to be vulcanised. This ensures an even filling up of the inner space of the frame under the pressure to which the pile of frames and plates is subjected before the steam is let in; the small excess of mixture that is placed in each frame has to be pressed out through the openings. Care is taken to cut the piece of mixture somewhat too large at first, and then bring it to the right weight by cutting off further slices. Adding weight to a too light piece of mixture in the form of small strips is only allowable when these pieces are placed along the borders, outside the place where the rings will have to be cut. Every place where two pieces of mixture have been joined together easily causes a weak place in the rings, probably from dust or dirt, so that joints should be avoided.

The steel plates between which the frames are put have not such a brilliantly hardened and polished surface that the vulcanisate is easily removed. After vulcanisation it sticks to the plates, and sometimes rather hard. As it is important to free the vulcanised slabs as soon as possible from the hot steel plates, to avoid after-vulcanisation and to make results as accurate as possible, we place pieces of tracing cloth between the mixture and the steel plates.

In former years we used thin sheets of lead; after use these can be flattened by beating and then pressing them in a heavy press, so that they can be used an indefinite number of times. The tracing cloth can be used only twice or sometimes three times, but is easier in the handling.

On the use of tracing cloth and sheets of block tin see B. J. EATON, Bull. F. M. S. No. 27 (1918), page 30.

Vulcanisation takes place in live steam, the autoclave press being fitted with an automatic steam-condensor, which allows the condensed water but very little steam to pass. A special pipe serves for blowing off the steam rapidly at the moment vulcanisation has to be broken off.

As vulcaniser we always use the autoclave press depicted in the foreground of Fig. 11. It has several advantages over the steam-autoclave seen behind it in Fig. 11, which we used in the beginning of our testing. In the first place the autoclave can only hold a relatively small number of moulds, the maximum being slabs for 34 rings in our case, while the pile of plates and frames in the autoclave press can easily be made high enough to contain the largest charge one would ever wish to place in it. The 90 to 95 rings which can be stretched in maximo on our Schopper machine in one day are easily vulcanised in one charge of the autoclave press, if desired. Further the operation of opening the press, taking out the vulcanisate and freeing it from the steel plates is much easier with the press, where no screws or bolts are used; the whole operation can be much more readily standardised than when using the screw-bolted pan with the heavy screw-moulds which it necessitates.

We may add that the lower part of the cover of our press, as well as the head of the piston, are hollow and provided with large holes, so that the steam can freely circulate above and below the pile containing the vulcanisate. Moreover we always add an extra plate with an empty frame both below and above the pile, to make conditions for the upper and lower slabs in the pile as much as possible the same as that of the slabs in the middle of the pile.

Nevertheless, differences caused by position in the vulcaniser may occur; pieces of the same slab of mixture, placed in different parts of the pile, may give slightly different results, the difference in length at 1.30 KG generally being only a few units and seldom exceeding 10 units.

Often the slabs placed in the lower parts of the pile, which are nearer to the steam-inlet, are somewhat further vulcanised than those placed in the upper parts; but a

constant difference could not be detected, and the deviations are mostly negligible.

We also compared the effect of the different steel frames used in our testing (small frames for slabs of two rings; larger frames for 6 rings; combined frames for 4 slabs each of two rings, see also § 199) but could not find a regularly recurring difference. Evidently the differences caused by such factors disappear amongst the accumulation of small errors of determination, the sum of which is a variation in length at 1.30 KG of ± 5 units, seldom increasing to ± 10 units.

The most even distribution of heat, and at the same time the most exact control of the temperature of vulcanisation is doubtless obtained in an oilbath; for very exact investigations, especially when different temperatures of vulcanisation have to be compared, the oilbath is probably to be preferred above every form of steam-autoclave. Its capacity however is much too small for our testing work, and when testing at one temperature only, the autoclave press yields excellent and sufficiently accurate results.

For the description of a glycerine bath for vulcanisation see D. SPENCE and J. YOUNG, Chem. Ztg. 36 (1912), 1162, and K. GOTTLÖB, G. Ztg. 30 (1916), 304; on the use of a bath of fused metal see A. O. BOURN, I. R. J. 45 (1913), 121. A special oilbath for vulcanisation is described in Comm. Delft V, page 138.

§ 215. Temperature of vulcanisation.

For comparative tests in one and the same institute an exact knowledge of the real temperature of vulcanisation is of no importance, at least when a constant temperature method is adhered to, as in our testing. Security as to an accurately constant reading of pressure gauge and thermometer is in such cases the only thing which has to be provided for; whether the real temperature is correctly indicated by the gauge or not, is of no influence in comparing the results. In addition to this we use a special method of controlling the constancy of temperature, which consists in adding a slab of one and the same control-sample to each vulcanisation (see § 216).

If results obtained in different institutes are to be compared, or if one institute uses several vulcanisers or different temperatures of vulcanisation, the exact temperature of vulcanisation must be gauged, the manometer and thermometer have to be controlled and their readings checked.

Reading of the steam-pressure is the most common method of controlling the temperature of vulcanisation. The advantage is that the pressure gauge indicates the real pressure current in the interior of the vulcaniser. A disadvantage is that the ordinary gauges are not very reliable, often rather inexact, and subject to changes from rust etc., so that they have to be controlled rather often, which means an interruption of the work, and necessitates a special control-apparatus.

Further the steam-pressure is not an exact gauge of the temperature, or better perhaps of the amount of heat supplied to the rubber-sulphur mixture; the amount of steam that is let off through the outlet-valve during vulcanisation, and even leakages for instance through the packing of the cover may influence the results. These factors may be controlled and regulated to a certain extent in one institute; but they are not easy to standardise, and it would be difficult to fix rules in such a manner that strictly comparable results are obtained in different institutes.

Moreover, the loss of heat by conduction and radiation may have a still unknown effect, and the form (dimensions, thickness of walls, etc.) of the vulcanising pan, as well as the type of frames or moulds used to put the mixture in, may influence the results, even if the steam-pressure and the amount of steam used are exactly the same.

Thermometer readings have the advantage that the thermometer can quickly and easily be controlled, for instance in vapours of boiling water, so that exact readings are easily obtained. On the other hand, the mercury column should not protrude much above the cover of the pan, and even then a rather large correction for the length of the mercury column has to be applied. Further, the thermometers supplied with the ordinary vulcanising apparatus generally reach only a slight distance into the interior of the pan,

and often do not protrude further than a hollow in the cover or side of the vulcaniser, where the temperature may be lower than in the middle. We use an ordinary accurate glass mercury thermometer, which is placed in a narrow iron pipe which protrudes some 15 cm into the interior of the vulcaniser, so that the mercury bulb of the thermometer is at the same height and close beside the pile of plates and frames which contains the vulcanisate. The temperature around this pipe may be assumed to be the same as that of the vulcanisate; but the thermometer itself, which in its upper part is in contact with the air, will eventually have a somewhat lower temperature, and the mercury column which rises just above the cover of the vulcaniser, so that it is just visible during vulcanisation, will also have a somewhat lower temperature, so that a (not exactly known) correction has to be applied. To facilitate the conduction of heat from the interior to the mercury we have sometimes filled the iron pipe around the thermometer with oil or small shot, but this did not afford any distinct advantage.

In vulcanisation we use both a manometer and a thermometer; the actual, corrected reading of the manometer is 4.3 atm. above atmospheric (61 lbs per square inch) which corresponds to a temperature of $153^{\circ}.2$ C ($307^{\circ}.8$ F). The reading of the thermometer, corrected for misreading of the instrument, is $150^{\circ}.5$ C. To this has to be added a small correction for the protruding mercury column, which is not indicated by the ordinary correction tables, but which may be estimated at about $0^{\circ}.4$. The temperature, as indicated by a thermometer placed as in our case (in a narrow iron pipe in the interior of the pan) would therefore be about 151° C (304° F) corr. The difference from the temperature as derived from the steam-pressure is $2^{\circ}.2$ C, which difference may be partly caused by the fact that the thermometer is not in direct contact with the steam. As stated above, neither steam-pressure nor thermometer reading seem to be a sufficient gauge of what actually takes place in vulcanisation, as the amount of steam that passes through the vulcaniser, the leakages, etc. are of influence on the results.

The following table gives the relation between temperature and steam-pressure.

Temperature Celsius	Temperature Fahrenheit	Pressure above atmospheric		
		KG per cM ²	atmospheres	lbs per square inch
130	266.0	1.76	1.67	25.1
135	275.0	2.20	2.10	31.4
140	284.0	2.70	2.58	38.4
142	287.6	2.91	2.78	41.3
144	291.2	3.13	3.00	44.5
146	294.8	3.37	3.23	47.9
148	298.4	3.61	3.47	51.4
149	300.2	3.74	3.59	53.2
150	302.0	3.87	3.71	55.0
151	303.8	4.00	3.84	56.9
152	305.6	4.14	3.97	58.8
153	307.4	4.28	4.10	60.8
154	309.2	4.42	4.24	62.9

In the neighbourhood of our temperature of vulcanisation
 1° C corresponds with 0.13 atmosphere and 1.9 lbs
 per square inch
 0.1 atmosphere „ „ 0°.77 C and 1.46 lbs
 per square inch
 1 lb per square inch „ „ 0°.53 C and 0.068
 atmosphere.

The influence of deviations in the temperature of vulcanisation may be judged from the following data:

for an ordinary sample of smoked sheet or crepe a deviation of 0°.1 C (0.2 lb per square inch) above or below the standard temperature (during the whole vulcanisation) decreases or increases the length at 1.30 KG by 3—4 units, and therefore decreases or increases the time of cure by about 1 minute ($\frac{3}{4}$ —1 %) and the coefficient of vulcanisation also by about $\frac{3}{4}$ —1 % or 0.04 units.

In starting our testing work we used the steam-autoclave seen behind the autoclave press in Fig. 11. We adopted a temperature of 148° C, the same as used in the Government Institute at Delft. The thermometer then in use had a mercury column which protruded rather far above the cover of the pan, to which

factor we did not pay attention at the time, so that no correction was applied and the real temperature must have been higher than 148°. Further, in changing over to the autoclave press (compare § 214), it was found that the temperature, as read on the same thermometer, had to be raised somewhat above that of the steam-autoclave (0°·9 C) to obtain exactly the same state of cure in the same time. This may be connected with many factors in the form of vulcaniser, the type of moulds and frames used to put the vulcanisate in etc. As will be described in § 216 we control our temperature of vulcanisation and keep it constant as far as possible by the regular use of control-samples; during the first years the real temperature was regarded as of minor importance, as long as exactly the same temperature was always used. Even to keep the same temperature was sometimes difficult, owing to the very inferior thermometers obtainable during part of the war. Only in later years have we determined the real temperature in our testing as accurately as possible, in connection with comparative tests with other institutes.

The ideal method for comparing in different institutes the actual temperature of vulcanisation, or better vulcanisation itself, would be to place some kind of temperature gauge in the middle between the slabs which are being vulcanised. Unfortunately the distance-thermometers now available seem either to be of too complicated a construction, or far from accurate enough at the high temperatures of vulcanisation.

Another expedient would be to use for comparison a chemical reaction which takes place at a convenient, measurable speed at the temperature of vulcanisation. The first reaction to be considered is, of course, that between rubber and sulphur themselves; standard samples of rubber might be exchanged and the temperature might be so adjusted in each institute that a certain coefficient of vulcanisation is reached in a certain time. In a certain way we use this method for our own control (see § 216); the drawback to it is that rubber is not a material of constant properties and that its rate of combination with sulphur may increase or decrease on keeping (compare § 163). Even in our elaborate control, using several separate control samples, we are not sure that the real temperature of vulcanisation has remained absolutely constant in the course of five years.

§ 216. Control of vulcanisation.

For accurate testing it is necessary to have a control of the execution of vulcanisation. Small deviations in the high temperature of vulcanisation may have a not unimportant effect on the results, as we saw in § 215; and a control of the rather tedious work of watching the thermometer and pressure gauge is necessary.

For this purpose we add to every charge of the autoclave press a slab (two rings) from one large control-sample, prepared by elaborately mixing and crepeing a sufficiently large quantity of homogeneous crepe. Such a control-sample lasts for 6 months to over a year. To make results as accurate as possible, we have in stock two or three control-samples of different rates of cure; one of these is quick curing and used for short cures; another has a time of cure of about 90 minutes and is used for intermediate cures, the third cures in 110 or 120 minutes and serves for the long cures. In this way the curves found for the control-slab never lie far from the standard curve, so that they can be easily and accurately compared with the average curve for the time of cure in question.

When a fresh control-sample has been prepared, slabs for two rings are added to every vulcanisation of the times of cure for which it will have to serve, besides the slab of the control-sample then in use; and thus the new sample is tested for one or two months, till the average figures (position of the curves) for different times of cure are obtained with sufficient accuracy. This is easily judged by comparing the position of the average curves for increasing times of cure: the difference for each interval of 5 minutes in time of cure must decrease regularly with increasing times of cure. Generally the length at 1.30 KG is determined from the figures for breaking point in the manner described in § 220, and the average length at 1.30 KG gives the position of the average curve. When sufficient accurate data have been obtained, sets of curves are drawn, using the slope of the upper part of the curve which corresponds with the figure for slope or type after SCHIDROWITZ as in the table on page 532 (§ 221).

One of these sets is reproduced in Fig. 22, for times of cure from 90 to 110 minutes; for this sample and two others the lengths at 1.30 KG for increasing times of cure are:

Quick curing control-sample		Intermediate control-sample		Slow curing control-sample	
Time of cure	Length at 1.30 KG	Time of cure	Length at 1.30 KG	Time of cure	Length at 1.30 KG
50	1054	90	1006	105	1068
55	1025	95	987	110	1048
60	1000	100	969	115	1030
65	976	105	952	120	1013
		110	936	125	997
				130	981
				135	966
				140	952

The decrease in length at 1.30 KG for an interval of 5 minutes becomes smaller, the more advanced the cure; this may also be clearly seen from Figs. 14 and 18.

In the neighbourhood of our standard curve (length at 1.30 KG 990 %) a difference in time of cure of 5 minutes causes the curve to come lower down 24 units for the quick curing sample, 19 units for the medium and 16 units for the slow curing sample. For 5 % of the time of cure the difference in length at 1.30 KG is 15, 18 and 20 units respectively.

The average figures for breaking load and final length of the two rings of the control-sample added to a certain vulcanisation are simply plotted in Fig. 22 and the vertical distance of this point from the average curve is read. Suppose that the control-slab used in a vulcanisation of 100 minutes gives a breaking point of 1.41^5 KG per mM^2 and 993 % length: then point B in Fig. 22 is found, $2\frac{1}{4}$ mM or $5\frac{1}{2}$ units in length above the average curve for 100 minutes. In another cure for 105 minutes point A (1.34 KG per mM^2 , 944 %) may be found, 15 units below the average curve.

In applying a correction we follow this rule: deviations smaller than 10 units in length are neglected, whilst half the value of larger deviations is used as a correction. The following considerations lead to this rule.

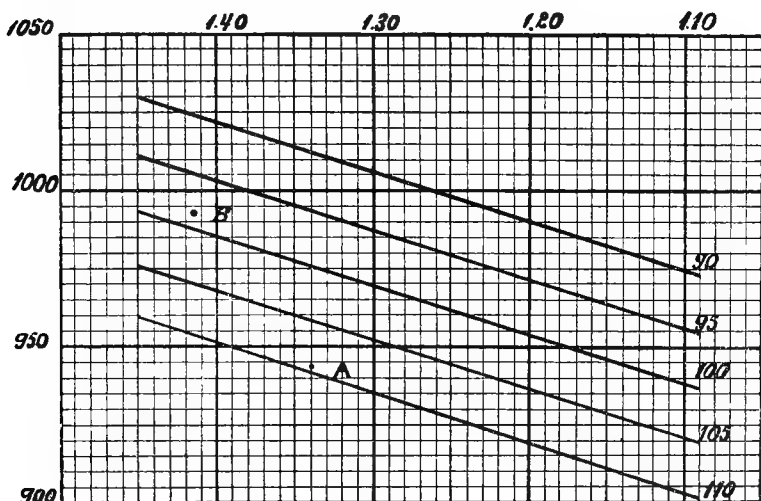


Fig. 22.

Upper part of stress-strain curves for cures with intervals of 5 minutes for one control-sample, used to determine the correction in vulcanisation.

The deviation from the average position of the curve may be caused by:

- 1) errors or deviations in the temperature of vulcanisation.
- 2) other factors causing experimental errors, such as differences in the mixture, the position in the vulcanising pan, the reading and calculating of testing results etc.

The first is the error for which it is intended to apply a correction by using the control-sample. Taking the full deviation of the control-sample as correction would mean assuming that this deviation is only caused by errors in temperature of vulcanisation, or in other words that all other errors are negligibly small when compared with this one. We have in former years applied a correction according to this rule. An extensive study of our data, especially of large series of figures for the deviations from the average curves of two control-samples, vulcanised side by side, then

led to the conclusion that other factors have approximately as large an influence as the errors in temperature, so that half the deviation found for the control-sample is the best value to use as a correction.

This correction is then simply added to or subtracted from the length at breaking (or, which comes to the same thing, the length at 1.30 KG) of every sample cured in that same charge. Some examples to illustrate this method of correcting errors in temperature of vulcanisation will be given in § 219.

§ 217. Keeping the vulcanised slabs before testing.

In the first few hours after vulcanisation the slabs undergo a very visible change. The hot slabs are more or less transparent; shortly cured samples, when held to the light, show a lively brown colour and are half transparent, so that an object moved along the far side is clearly distinguishable. The further advanced the cure, the more the colour takes on a lead-blue or -black tint, and the less transparent the still hot slab is.

Soon after the slabs have cooled down a change sets in; especially in shortly vulcanised slabs the difference is very marked, they become grey-brown and wholly untransparent, and the transition can be easily followed, untransparent patches being formed here and there and spreading like blots till the whole slab has changed. Probably some form of separation of the sulphur (from the dissolved or fused to the solid state) takes place; but this has not yet been followed up in detail.

After further keeping the slabs undergo the gradual changes described in § 209 as „ageing”; to obtain strictly comparable results, the time between vulcanisation and testing must therefore be standardised. Testing old slabs would mean a lower lying stress-strain curve, therefore apparently a shorter time of cure, further eventually a smaller tensile strength and a somewhat higher coefficient of vulcanisation, in proportion as the changes described in § 209 have advanced.

The changes in the first few days after vulcanisation are not very large; the stress-strain curve may come down some 1—2 units in length at 1.30 KG per day, which would mean a decrease in time of cure of about $\frac{1}{2}$ minute per 24 hours keeping.

Nevertheless, to obtain strictly comparable results it is better once and for all to fix the time between vulcanisation and testing, which procedure has further evident advantages in mass-work and routine testing. In the first years we adopted a period of 3 times 24 hours between vulcanisation and testing, so that the slabs vulcanised on Monday were tested on Thursday, and so on. This interval was chosen by many investigators, so as to allow the slabs to come to complete rest and equilibrium after the heavy disturbance caused by vulcanisation.

A large number of comparative tests however then proved that a rest of 24 hours gives quite as reliable results. A keeping period of only 24 hours has the advantage that the testing results are known earlier, and further that the administration of the samples and results is more simple; in consequence we have adopted this interval for our testing work. Of course the slabs vulcanised on Saturday can only be tested on Monday; this gives a small irregularity, which for ordinary samples falls within the limits of error, and which for very accurate investigations can be avoided.

See O. DE VRIES and W. SPOON, Arch. 2 (1918), 814; also I. R. J. 57 (1919), 78. Further O. DE VRIES, I. R. J. 53 (1917), 101.

H. P. STEVENS (J. S. Ch. I. 35 (1916), 872) drew special attention to the importance of fixing the period between vulcanisation and testing. He (J. S. Ch. I. 37 (1918), 280 T) generally found the load at 10 or 9 times the original length for samples kept 7 days after vulcanisation to be greater than for samples tested 24 hours after vulcanisation, exceptions (probably due to experimental errors) however occurring.

It may be added that the downward movement of the stress-strain curve seems to be larger during the first hours after vulcanisation, so that testing a few hours after vulcanisation may give a 20 units greater length at 1.30 KG than testing 1 day after vulcanisation. This point is interesting in connection with the disintegrating action of heat in general, which tends to increase the length at a certain load (makes the rubber weaker). It seems as if during the first few

hours a real hardening takes place after the rubber has cooled down. Tests on freshly vulcanised, still hot rubber would be of importance to study this hardening of the slabs as they restore themselves after vulcanisation.

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 52 (1916), 617) found testing $\frac{1}{2}$ or 2 hours after vulcanisation to give a somewhat greater length at a load of 0.60 KG per mM^2 than testing after 24 or 72 hours, the difference amounting to 8–24 units in length.

The temperature at which the slabs are kept between vulcanisation and testing has some influence on the results. The higher the temperature, the more rapid the ageing phenomena proceed. The variations in temperature in the Buitenzorg climate are, however, so small that they have not the least influence on the results. For European circumstances with a larger variation between summer and winter this point seems of some importance.

H. P. STEVENS (J. S. Ch. I. 37 (1918), 280 T) found a rather large difference in load at 9 or 10 times the original length, when keeping the vulcanised slabs at 10° or at 30° , amounting to 0.05–0.25 KG per mM^2 . Contrary to what one would expect, this difference was the same and even often smaller when the slabs were kept 7 days after vulcanisation instead of testing them 1 day after vulcanisation.

STEVENS proposed (ibid. page 284 T) to adopt a temperature of 30° C for keeping the specimens after vulcanisation, and to test them after 24 hours.

We did not find any difference in tensile strength or position of the curve when keeping the vulcanised slabs 3 days either in an ice-chest (temperature some 20° C) or in a cupboard in a cool room (temperature 26– 27° C) or in a warm place in the boiler-room (temp. 30 – 32° C). The extremes of room-temperature in Buitenzorg seldom reach these values.

Other conditions, such as the degree of moisture of the atmosphere, may have an influence on the results. Keeping the same samples after vulcanisation in a desiccator above quicklime or above water did not give a difference in tensile strength or slope; the position of the curve was generally lower (some 15 units, giving a difference of 5 minutes in time of cure) for the samples kept in a dry atmosphere, which therefore apparently cured quicker than those kept in the air or in a moist atmosphere above water.

The ordinary changes in moisture-content in our testing-room, however, do not seem to be of influence on the results.

Whether the rings are punched from the vulcanised slabs shortly before testing (as we generally do, punching early in the morning the rings that will have to be tested during that day) or on the foregoing day; whether the rubber is stored in the form of rings or of unpunched slabs, does not cause a difference in the results, as far as our tests go.

§ 218. Testing the vulcanised rubber.

The vulcanised slabs of one day are kept in piles in the air till the next morning; rings are then punched with a Schopper punching machine with circular knives, which may be seen on the table in Fig. 12.

Compare also Bull. F. M. S. No. 27 (1918), plate 16, page 20, and description *ibid.* page 18.

The breadth of the rings varies between 3.7 and 3.8 mM in our case and is not accurately the same over the whole circumference. Though we closely investigated this point, we could never find that the rings break by preference in the thinnest part; the breaking points are regularly distributed over the broader and smaller parts. The accidental factors which cause a fissure to start and lead to a break seem to be independent of the greater strain per mM^2 in the thinner parts of the rings, probably because the rings are constantly revolved on the Schopper machine. We therefore adopt an average breadth of 3.75 mM for all our rings and do not measure the breadth of each ring separately.

The thickness of the rings may vary somewhat; it generally lies very near 5.0 mM, and seldom deviates more than 0.15 mM on either side. It is measured on the inner disk which remains after cutting the ring. The thickness gauge may be seen in Fig. 12 to the right; the thickness is read in hundredths of a millimeter. Thickness $\times 3.75 \times 2$ gives the cross section of the ring, by which the total load at breaking is divided to obtain the load in KG per mM^2 .

The Schopper stretching apparatus (see Fig. 12) gives a direct reading for the breaking load in KG and the elongation in % of original length. These figures, recorded by the native boy in charge of these tests, may be controlled by the autographically drawn curves, the abscissae of which indicate the weight ($1 \text{ mM} = 0.4 \text{ KG}$ total weight) and the ordinates the elongation ($1 \text{ mM} = 5 \%$ elongation).

The zero position of the weight lever is obtained by adjusting the screw in the foot of the apparatus and bringing the machine to an exactly vertical position. The zero-point of the elongation-scale has to be adjusted so that it passes the mark of the nonius at the moment the ring is stretched to its „original length”. This point is subject to different interpretations, as the ring is already stretched to a small extent when the parts of the ring between the rollers have reached a straight, vertical direction. We prefer to fix the zero-point of the scale by the following calculation. The inner diameter of the rings is $44\frac{1}{2} \text{ mM}$ and the inner circumference therefore 140 mM . The rollers of the stretching machine on which the rings are put have a diameter of 25 mM ; half the circumference is therefore $39\frac{1}{2} \text{ mM}$ and the part of the ring that covers the upper half of one, and the lower half of the other roller amounts to 79 mM . Therefore 61 mM remain for the two vertical parts, so that the zero-point of the scale must pass the nonius when the centers of the two rollers are $30\frac{1}{2} \text{ mM}$ apart.

If the adjustment of the zero-point of the scale is not exact, the autographically drawn curves show a vertical part of some millimeters below the small bend that indicates the moment that the ring begins to stretch, which gives a small shock to the weight lever.

The speed at which the rings are stretched is of some influence on the results. It may be regulated by the tap which controls the water supply. We have adopted the following speed:

250 %	elongation to be reached in 30 seconds					
500 %	”	”	”	”	61	”
750 %	”	”	”	”	93	”

The curves depicted in Fig. 13 and 14 are rather smooth. Often the curves obtained on the Schopper machine show

smaller or larger oscillations, according to whether the machine runs more or less smoothly. The rollers on which the rings, during stretching, are revolved have to bear a great strain, and when the machine is in constant use, as in our testing work, the axles and ball-bearings gradually wear out. This makes itself felt in a less smooth form of the curve, caused by a kind of hysteresis, the rings stretching to some extent before the upper loose roller follows the revolution of the lower one.

The Schopper machine can also be used without the weight on the lever; the curve is then stretched out in horizontal direction and takes a less steep form. We have not found any advantage in using this form of curve, while of the steeper curves a larger number can be drawn together on one piece of paper.

We have not made investigations with other testing machines for which the rubber has to be cut in the form of strips. As to the objection, often raised against the use of ring-shaped test pieces, viz. that the outer circumference is stretched to a percentually smaller degree than the inner one, we may remark that the rings on the Schopper machine during stretching often topple over on their side on one of the axes, so that they show a half twist, without this giving any difference in the results. We have counted the number of beginning fissures, which did not lead to the break, in five hundred broken rings, and found 314 fissures on the outer against 353 on the inner circumference, so that the break shows no preference in starting on one side rather than on the other.

The temperature at which the rings are stretched has a decided influence on the results, a higher temperature increasing the elongation and decreasing the tensile strength, so that the curve comes to lie higher on the paper and the rings break earlier. In accurate testing measures should be taken to keep the room-temperature during stretching as nearly as possible the same.

See P. L. WORMELEY (Rubb. Ind. 1914, page 249, and Circular Bureau of Standards (Washington) No. 38 (1915), page 37) for temperatures of 10, 21 and 32° C.

The extremes of room-temperature in temperate zones may have an appreciable influence on the testing results.

In this respect we are in a favourable condition; the variation in room-temperature both from the early morning to midday, and in different seasons, is never more than 4 or 5 degrees Celsius. The average room-temperature in Buitenzorg is 27°.5 C; temperatures below 26° or above 30° very seldom occur.

As to the influence of the moisture-content of the atmosphere during testing data are still scarce. The degree of moisture in Buitenzorg may vary considerably from the dry to the wet monsoon, for instance from about 60 to 90 or 95%. We have not yet been able to make a special study of the influence of this factor; a cursory survey of figures does not reveal any special difference which must be ascribed to testing in the dry or the wet monsoon.

§ 219. Determination of breaking point, tensile strength and standard time of cure.

In regard to the interpretation of the figures for breaking load a difference of opinion still reigns. Some authors take as breaking load the highest figure obtained for any one of the rings tested; they argue that every lower figure is caused by some flaw or particle of dirt, and that only the best ring shows, or at least approximates, the real strength of the rubber. Others prefer to calculate the average figure for all the rings tested, rejecting only those rings that give abnormally low figures, or in which some disturbing factor (air-bubble, piece of dirt) can actually be demonstrated.

Perhaps a mathematical study of a large number of figures for breaking points of slabs from one sample, cured for the same time (such as obtained with our control-samples), might lead to a conclusion as to the best and most scientific interpretation of these figures; such a study, however, is still lacking.

See the arguments of K. GOTTLÖB (G. Ztg. 30 (1916), 307) for adopting the value for breaking load of the best ring only.

B. J. EATON and his co-workers (Bull. F. M. S. No. 27 (1918), 45) usually test two rings, and take the figures from the better ring. A single such test, of course, gives very doubtful results, owing to the fortuitous character of the breaking point; average figures for a series of such tests may however give more reliable data.

For an ordinary sample we generally test four or six rings, and take the average breaking load of these rings, with the exception of those which evidently give largely deviating figures, for instance a breaking load that is 0.20 KG per mm^2 or more smaller than that of the other rings. The length at breaking is the average of the lengths of the same rings as used in the determination of breaking load.

As we mentioned in § 218, the breadth of the rings is always taken at 3.75 mm; the thickness is measured for each ring, and the breaking load per mm^2 is calculated by dividing the load actually found in KG by $2 \times 3.75 \times \text{thickness}$. As an example we copy the following data from our file (in which every sample has its own card to register all vulcanisation-data).

Slope $35\frac{1}{2}$				Sample 1933 Q					
Tested	Cured for	Number of ring	Number of graph	Elongation at breaking	Breaking load	Thickness of ring	Length at breaking	Load in KG per mm^2	Average and correction
17/3 '20	105 min.	1	6875	883	55.0	5.00	983	1.46 ⁵	} 1.41 978 corr. 986
		2		873	50.6	4.95	973	1.36	
22/3 '20	100 min.	1	6895	905	51.4	4.95	1005	1.38 ⁵	} 1.38 1010
		2		918	53.0	5.00	1018	1.41 ⁵	
		3		910	50.8	4.91	1010	1.38	
		4		899	49.4	4.95	999	1.33	
		5		905	49.3	4.96	1005	1.32 ⁵	
		6		922	53.8	4.92	1022	1.45 ⁵	

For the first vulcanisation the control-slab gave 1.34 KG per mm^2 with a length of 944 $\%$, point A in Fig. 22. This point lies 15 units in length below the average curve for 105 minutes, that is the vulcanisation was too far advanced by nearly 5 minutes (perhaps the temperature was taken somewhat too high). This difference of 15 units in length can be derived graphically, by plotting A on millimetric paper as in Fig. 22 and reading the vertical distance from A to the curve 105. It can also be calculated by taking the length at 1.30 KG from the table on page 529, which (as the slope of the control-sample was 38) is found to be $944 - 6.4 = 938.6$. Subtracted from the average length at

1.30 KG for 105 minutes, which is 952 (see table on page 516), this gives a difference of $14\frac{1}{2}$ units in length. Half of the deviation of 15 units for the control-sample is taken as correction (see § 218); the corrected breaking length for sample 1933 Q therefore is $978 + 8 = 986$, and from the figures 1.41 and 986 a length at 1.30 KG of 970 is found from the table on page 529, the slope of sample 1933 Q being $35\frac{1}{2}$. This is 20 units in length lower than the standard (990 ‰), so that the trial vulcanisation was appr. 5 minutes too long. The sample has therefore a time of cure of approximately 100 minutes.

A vulcanisation of 100 minutes took place on the 22 March, and a slab of six rings of sample 1933 Q was added. The control-sample gave 1.41⁵ and 993, point B in Fig. 22, which lies $5\frac{1}{2}$ units above the average curve for 100 minutes (also, calculating from length at 1.30 KG, $993 - 18\frac{1}{2} = 974\frac{1}{2}$ or $5\frac{1}{2}$ above 969, the average for 100 minutes of the control-sample), for which deviation, being less than 10 units, no correction is applied.

The average breaking load of sample 1933 Q of 1.38 KG per mM^2 and the average length at breaking of 1010 give a length at 1.30 KG of 998 ‰, so that the standard time of cure is somewhat more than 100 minutes. The figures for this sample are therefore found to be:

Tensile strength	1.38 KG per mM^2
Standard time of cure	> 100 minutes
Slope	$35\frac{1}{2}$

In our regular routine testing three vulcanisations are mostly done every day, and 60 to 90 rings tested daily, of which some 6 belong to the control-samples. This means some 20000 rings per year, and a considerable amount of administration is of course involved, while a large number of calculations have to be done. These however can be well entrusted to our native clerks, and the control by European assistants is relatively easy and does not take too much time.

§ 220. Determination of the length at 1 30 KG.

For a certain sample of rubber the stress-strain curve has a definite form for every state or cure. This form

is, however, influenced by the „slope” or „type”, and may somewhat differ for different samples (compare Fig. 18).

The *position* of a certain curve for a given sample is therefore fixed by one point, for instance the breaking point, or the load at a certain elongation. The *form* of the curve has to be expressed by two points (as in the determination of slope, compare § 200) or by the direction or slope of, for instance, its upper part.

The form of the stress-strain curve represents a special property of the rubber, which we express as „slope” and discussed in § 200, 202 and 221. The position of the curve is an indication as to the state of cure.

The position of a curve for a certain sample is sufficiently fixed by the breaking point, e. g. the figures for breaking load and length at breaking. These figures are however not suitable for making comparisons between different samples, as both breaking load and length at breaking change with the state of cure, so that the relative positions of different breaking points can only be judged by plotting them on squared paper. In our method we compare the position of different stress-strain curves by the length at a load of 1.30 KG per mm^2 . This means comparing the points of intersection of a bundle of curves as in Fig. 14 or 18 with a vertical line, or in other words determining their vertical distance. Of course other vertical secants may also be used, and in special cases, when the tensile strength is low, we use the lengths at 1.20 or 1.10 KG for comparison. If a less advanced state of cure, in which the upper part of the stress-strain curve has a more or less vertical direction, is chosen as a basis for comparison, a horizontal secant is more suitable, and a comparison may be made between the loads at 900, 950 or 1000 % of the original length.

See for instance Comm. Delft V, page 154, where an elongation of 850 % or a length of 950 % is chosen.

H. P. STEVENS (Bull. R. G. A. 1 (1919), No. 1, page 37) uses elongations of 800 and 900 %; D. F. CRANOR (I. R. W. 61 (1919), 137; also I. R. J. 58 (1919), 1199) mentions the loads at 600 %, 700 % and 800 % elongation.

The length at 1.30 KG may be determined in several ways. The first is to read it directly by covering the graph

obtained on the Schopper machine with transparent squared paper, on which the vertical line for 1.30 KG is drawn, and reading the length much in the same way, therefore, as will be treated for slope in § 221. We never use this method, as the length has then to be determined separately for every curve (every ring tested), taking into account the thickness of the ring, and calculating the average of the figures obtained in this way.

It is more simple to determine the length at 1.30 KG directly from the average breaking point of the rings tested, in the calculation of which the thickness of the rings has already been taken into account (see § 219). This breaking point may be plotted on squared millimetric paper, taking 0.1 KG load = 1 mM horizontally, and 5 units in length = 1 mM in vertical direction or, better still, double that scale. With the dimensions of the rings and of the autographic apparatus used on the Schopper machine this scale gives the same ratio between ordinates and abscissae as in the autographically obtained stress-strain curves; the slope of the upper part of the stress-strain curve may be copied directly on the millimetric paper either by the aid of ordinary wooden drawing-triangles or by using sufficiently transparent millimetric paper, which is put in the right position on the graphs. The part of the stress-strain curve from the breaking point to a load of 1.30 KG being copied in this way, the length at 1.30 KG can be read directly.

This method only gives correct results if the cross-section of the rings is accurately 4×5 mM. In our case the breadth of the rings is only 3.7—3.8 mM, and this means that the stress-strain curve obtained on the Schopper machine is compressed (shortened) in the direction of the abscissae, so that 0.1 KG load is represented by less than 1 mM on the paper, in fact by $\frac{3.75}{4} = \frac{15}{16}$ mM. Taking the slope directly from the paper therefore means tracing the upper end of the stress-strain curve somewhat too steep. For breaking points not too far from 1.30 KG the difference is small and may be ranked amongst the unavoidable errors in ordinary testing; for exact investigations this point has however to be taken into account.

We have used this graphical method for a long time, but

have now replaced it by a simple calculation from the following table, which contains the units in length to be added to or subtracted from the length at breaking (depending upon whether the breaking load is smaller or greater than 1.30 KG per mm^2).

Reduction of breaking length to length at 1.30 KG.

Breaking load		Slope				
		34	36	38	40	42
1.31	1.29	1.4	1.5	1.6	1.7	1.8
1.32	1.28	2.7	3.0	3.2	3.5	3.7
1.33	1.27	4.1	4.5	4.8	5.2	5.5
1.34	1.26	5.5	6.0	6.4	6.9	7.4
1.35	1.25	6.9	7.5	8.1	8.7	9.2
1.36	1.24	8.2	8.9	9.7	10.4	11.0
1.37	1.23	9.6	10.4	11.3	12.1	12.9
1.38	1.22	11.0	11.9	12.9	13.8	14.7
1.39	1.21	12.3	13.4	14.5	15.6	16.6
1.40	1.20	13.7	14.9	16.1	17.3	18.4
1.41	1.19	15.1	16.4	17.7	19.0	20.2
1.42	1.18	16.4	17.9	19.3	20.7	22.1
1.43	1.17	17.8	19.4	20.9	22.5	23.9
1.44	1.16	19.2	20.9	22.5	24.2	25.8
1.45	1.15	20.6	22.4	24.2	25.9	27.6
1.46	1.14	21.9	23.8	25.8	27.6	29.4
1.47	1.13	23.3	25.3	27.4	29.3	31.3
1.48	1.12	24.7	26.8	29.0	31.0	33.1
1.49	1.11	26.0	28.3	30.6	32.8	35.0
1.50	1.10	27.4	29.8	32.2	34.5	36.8

With the aid of this table the length at 1.30 KG is directly deducted from the figures for the breaking point. The „slope” of the sample, which is an expression for the form of the curve, and connected with the slope of the upper end of the stress-strain curve (see § 221) has to be taken into account for this calculation. For practical purposes an abbreviated table is used, which gives sufficiently accurate data and runs as follows:

Breaking load		Correction for trial vulcanisation	Correction for final vulcanisation		
			Slope 33—36	Slope 36—38	Slope 39—41
1.32	1.28	3	3	3	3 1/2
1.34	1.26	6	5 1/2	6	7
1.36	1.24	9	8 1/2	9 1/2	10 1/2
1.38	1.22	12	11	12 1/2	14
1.40	1.20	15	14	15 1/2	17 1/2
1.42	1.18	18	17	18 1/2	20 1/2
1.44	1.16	21	19 1/2	21 1/2	24
1.46	1.14	24	22 1/2	25	27 1/2
1.48	1.12	27	25	28	31
1.50	1.10	30	28	31	34 1/2

In this way the determination of the length at 1.30 KG becomes a very simple calculation, which is done at the same time as the calculation of the average corrected figure for breaking point (see § 219).

The length at 1.30 KG gives the position of the curve and the state of cure; if it is near enough to 990 ‰, the standard time of cure may be directly deducted from it.

§ 221. Determination of slope.

The slope, after the definition given by SCHIDROWITZ and GOLDSBROUGH, is $0.4(\text{length at } 1.04 \text{ KG} - \text{length at } 0.60 \text{ KG})$. It is determined graphically from the curve obtained on the Schopper machine.

A thin, sufficiently transparent sheet of squared millimetric paper is placed in the right position on the curve. On this millimetric paper two vertical lines are drawn at horizontal distances of 56.3 and 97.5 mM from the origin; these represent loads of 0.60 KG and 1.04 KG per mm^2 , as the rings in our testing have a breadth of 3.75 mM and not 4 mM, so that the figures for load have to be reduced to $15/16$. The vertical distance of the points where the Schopper curve cuts these lines is read in mM, and as 1 mM on the Schopper diagram is 5 units in length, this vertical distance in mM, multiplied by 2, gives the figure for slope. If necessary the

slope is determined for curves of several of the rings tested, and the average taken.

This graphical determination would be very simple and easy, were it not that the curves obtained on the Schopper machine are never quite smooth, but show small oscillations, which may even become rather large when the machine is long in use and the axles and ball-bearings have become somewhat worn. An average curve may then be adopted to determine the points of intersection; but this makes the results somewhat less accurate. Further the curve as it is drawn by a somewhat blunt pen has a certain breadth; care must be taken, when reading the vertical difference, to use in both cases the upper (or the lower) border of the line.

An experienced operator reads the slope with no larger error than $\frac{1}{2}$ unit, which is the limit we give in our tests. By repeat tests and repeated readings a greater degree of accuracy can, of course, be obtained if desired.

In the determination of slope it should be taken into account that the slope is not the same for curves for different states of cure. The longer the cure, the greater the figure for slope, the stress-strain curve losing more and more its shoulder, as may be seen from Figs. 14 and 18. For a sample with a slope of 36 the figures may be:

Length of curve at 1.30 KG	1070	1050	1030	1010	990	970	950
Slope	34.7	35.1	35.4	35.7	36.0	36.3 ⁵	36.7

For curves in the neighbourhood of the standard curve, as they are used in our ordinary testing, the difference is therefore only a few tenths of one unit, that is less than the ordinary error of determination.

For the study of the form of the stress-strain curve of rubber it is interesting to remark that the slope determined in the above described manner shows a relationship with the actual slope of the straight upper part of the curve. Expressing the latter, as it is obtained on the Schopper machine, in ‰ (which corresponds with the difference in length for an increase in load of 0.20 KG) the figures for our standard curve are:

Slope (after SCHIDROWITZ)	33	34	35	36	37	38	39	40	42
Slope of straight upper part	26.3	27.5	28.7	29.9	31.1	32.2	33.4	34.6	37.0

These figures hold for standard curves, for which the length at 1.30 KG is 990 %.

The curves for increasing times of cure take a more and more horizontal direction in their upper part, as may be clearly seen from Figs. 14 and 18. Taking the same example as above with a slope of 36, the figures for the straight upper end of the curves for successive cures are:

Length at 1.30 KG	1070	1050	1030	1010	990	970	950
Slope of upper part (difference in length for 0.20 KG increase in load)	33.6	32.2	30.8	30.1	29.9	29.7	29.5

Further discussion of the form of the stress-strain curves and their possible relation to conchoidal curves see PH. SCHIDROWITZ, H. A. GOLDSBROUGH and E. HATSCHEK, J. S. Ch. I. 38 (1919), 347 T.

§ 222. Determination of other properties.

Permanent set.

For the determination of permanent set rings of the same dimensions are used as on the Schopper machine. These rings are stretched on a glass plate with rounded edges (breadth 34 cM, thickness 8 mM), so that the rings are stretched to five times their original length (inner diameter of rings 44 1/2 mM, half inner circumference 70 mM).

One corner of the glass plate is cut obliquely to facilitate putting on and taking off the rings. The rings remain stretched for 24 hours, the length is measured before stretching and six hours after they have been taken from the glass plate.

For measuring the length of the ring a Schopper measuring apparatus is used, on which the rings are stretched with a total weight of 200 gms (10 gms per mM²) and the length read in tenths of a millimeter with the aid of a nonius. We take the precaution to put the ring on the glass plate in a fixed position with a mark (the series

number of the ring) in the middle between the edges, and to put it on the measuring machine in exactly the same position before as after stretching, with the mark below. This tends to avoid errors due to small differences in the breadth of the ring or to slight unevenness of the inner surface, and to the greater strain the ring has undergone on the edges of the glass plate. The reading of the length is more or less conventional, as the ring keeps on stretching slowly under the applied weight of 200 gms; even the way in which the weight is applied (smoothly or abruptly) has an influence on the results. A certain method has to be chosen and adhered to; we read the length immediately after the ring has come to apparent rest after letting down the weight slowly. Provided that the readings are effected in the same manner before and after stretching on the glass plate, the difference in length (which gives the figure for permanent set by dividing it by 70 mM, the original length of the ring) can be obtained with sufficient accuracy. It should however not be forgotten that single determinations only give a degree of exactness of about $\frac{1}{2}$ unit (0.5 in permanent set corresponding with only 0.35 mM difference in length before and after stretching). To obtain reliable results several rings should always be tested.

It is interesting to remark that the state of cure of the rings makes itself already felt when measuring their length before putting them on the glass plate. This length is about 1 mM greater for under-vulcanised than for far-vulcanised slabs. That permanent set is also dependent upon state of cure, and decreases as the rubber has been farther vulcanised, was discussed in § 207.

Using the same rings for permanent set determinations and afterwards for stretching on the Schopper machine is not allowable; the vulcanisate is weakened by the stretching, and on the Schopper machine a curve in a higher position (greater elongation for a certain weight) is obtained.

The above is the method prescribed by the Government Institute at Delft (Comm. Delft V, page 171). See further O. DE VRIES and H. J. HELLENDORF, *J. S. Ch.* 1. 36 (1917), 1258. The measuring apparatus is depicted for instance in *Bull. F. M. S.* No. 27 (1918), plate 21, page 25.

Coefficient of vulcanisation.

The coefficient of vulcanisation is determined in the main after the prescription of the Government Institute at Delft (*Comm. Delft V, page 143*). Extraction of the free sulphur is effected either in a Soxhlet apparatus for twice 8 hours, or in a Berntrop apparatus, leaving the paper thimble which contains the finely cut vulcanisate for 6 hours in the boiling acetone and afterwards 2 hours in its vapour and below the reflux to wash it out.

The oxydation of the sulphur in the extracted rubber is done with magnesium nitrate and nitric acid in the manner described in the above mentioned prescription.

CHAPTER XIX.

OTHER METHODS OF TESTING.

In this chapter we will compare the advantages and disadvantages of different methods of testing, and the reasons that have led us to adopt the method described in the foregoing pages. A complete review of all that has been done in the matter of rubber-testing does not lie within our object and would lead us much too far; we will touch on only those points that are closely connected with the testing of raw rubber and the investigations as to preparation and properties of plantation-rubber described in this book.

§ 223. Different content of sulphur.

For the testing of raw rubber in mixtures of rubber and sulphur only a content of between $7\frac{1}{2}$ and 10 % sulphur is usually chosen (compare § 224, page 546); in technical mixings the sulphur-content goes down to 3 %. Mixtures with more than 10 % sulphur, as used for instance in the manufacture of hard-rubber goods, can be left out of consideration here.

The influence of the sulphur-content on the properties after vulcanisation is depicted schematically in Fig. 23, in which the thick curves represent the breaking points for successive cures. The curve for a mixture with $7\frac{1}{2}$ % sulphur corresponds with those in Figs. 14 and 18; it shows the maximum of tensile strength and then goes down regularly and in such a manner that each subsequent stress-strain curve lies below the foregoing, so that the stress-strain curves for increasing times of cure show a regular downward movement. With mixtures containing 6 % of sulphur the first part of the curve of breaking points, up to the maximum of tensile strength, has nearly the same form as

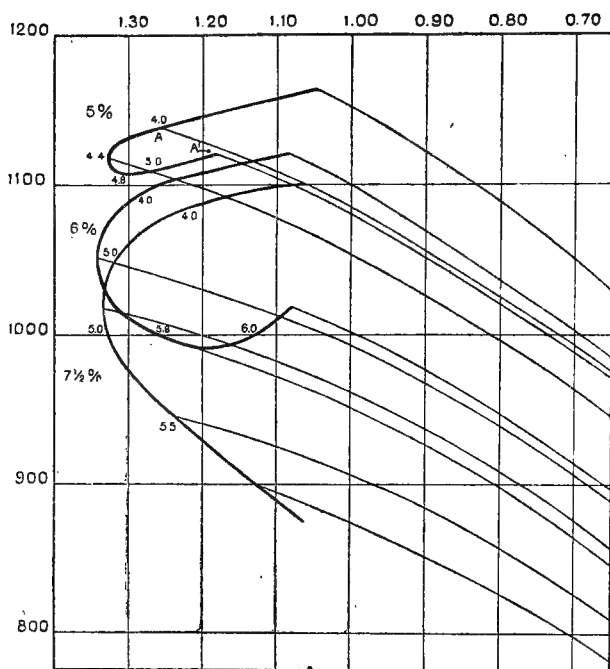


Fig. 23.

Curves of breaking points and maximum of tensile strength for mixtures with 5 %, 6 % and 7 $\frac{1}{2}$ % of sulphur. The content of combined sulphur (as percentage of the mixture) is added for different states of cure.

for mixtures with 7 $\frac{1}{2}$ % sulphur; in further vulcanisation the curve for breaking points at first continues to go downwards but then goes upwards again, so that the stress-strain curves proceed further down at first, but then show a retrograde, upward, movement. This lowest position of the stress-strain curve is reached when approximately the whole of the sulphur has gone into combination with the rubber: further heating then cannot cause any further combination of rubber and sulphur, but has only the disintegrating effect of heat, by which the vulcanisate becomes weaker and gives a greater elongation for a given load. In the mixture with 7 $\frac{1}{2}$ % sulphur the region where all the sulphur is used up cannot be studied in this way, as the rubber is over-vulcanised and completely brittle before all the sulphur has gone into combination, so

that no stress-strain curves for such a state of cure can be obtained.

The backward movement of the stress-strain curve is still more clearly seen with mixtures containing 5 % of sulphur; the loop in the curve of breaking points is narrower (see Fig. 23). When comparing two stress-strain curves in the same position, such as OA and OA' in Fig. 23, one for a vulcanisate with a figure for combined sulphur of 4.0, and the other for a vulcanisate which has already passed the maximum of tensile strength and in which all the sulphur has combined with the rubber (combined sulphur 5.0), the tensile strength is smaller for the latter one (breaking point A' as compared with A), clearly showing the deteriorating effect of prolonged heating.

Mixtures with only 3 % of sulphur could not be tested in this way, as the rings do not break at the maximum elongation (1125 %) obtainable on our Schopper testing machine. The forward and backward movement of the stress-strain curve could however be clearly determined also in this case by comparing the loads at a fixed length.

See O. DE VRIES and H. J. HELLENDORF, Arch. 2 (1918), 769; compare also J. S. Ch. I. 38 (1919), 91 T and I. R. J. 57 (1919), 1163.

These data can be arranged in another way by plotting breaking load and length at breaking against time of cure. For samples with 10, 7 $\frac{1}{2}$ and 5 % sulphur cured at 140° this is done in Fig. 24. The curve for 10 % sulphur presents a rather steep peak and a small summit; the summit for a 7 $\frac{1}{2}$ % mixture is broader and lies more to the right, while for the 5 % mixture the maximum tensile strength is not yet reached in 4 $\frac{1}{2}$ hours cure, and the maximum will be very flat.

See also the curves for mixtures of Para-rubber with 3 to 10 % of sulphur and an accelerator (vulkacit) by K. GOTTLOB, G. Ztg. 30 (1916), 326; further B. J. EATON and J. GRANTHAM, J. S. Ch. I. 35 (1916), 1046, and Bull. F. M. S. No. 27 (1918), page 120, diagram 28.

Whether the amount of sulphur in the mixture has an influence on tensile strength, is not yet certain. The example given in Fig. 23 indicates the same maximum tensile strength

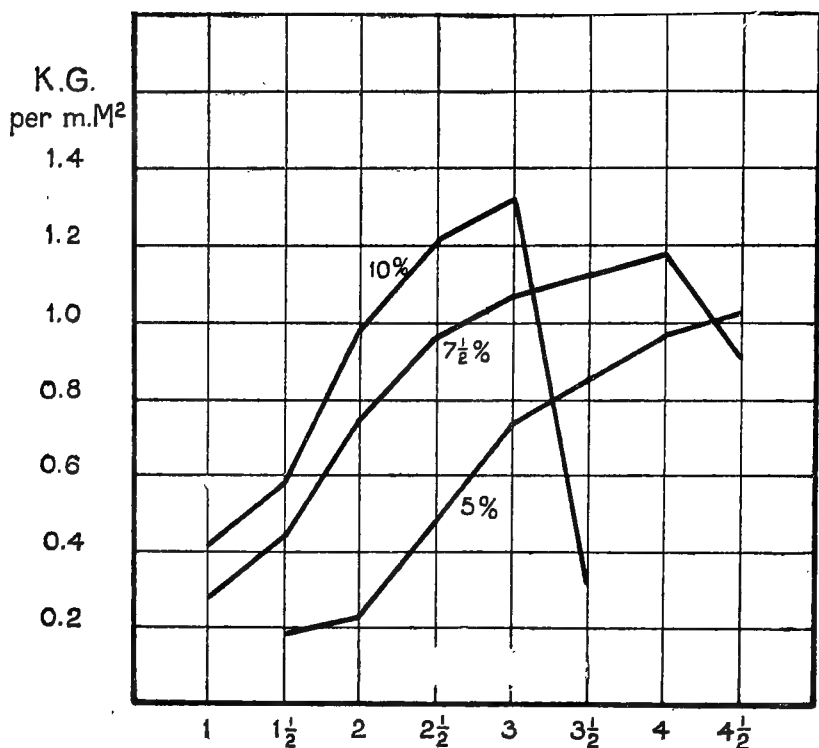


Fig. 24.

Breaking load plotted against time of cure in hours for mixtures with 5%, 7½% and 10 % of sulphur.

for mixtures with 5 to 7½% of sulphur. Whether this is a general rule would have to be determined by more elaborate investigations.

K. GOTTLOB (G. Ztg. 30 (1916), 326) found the maximum tensile strength (taken from only the best rings) approximately the same for mixtures containing 1 part vulkacit and 6 to 10 parts of sulphur on 100 rubber. For 5 parts of sulphur and less the maximum value for tensile strength was found to be smaller.

P. BREUIL (C. Gp. 1906, page 558), on the contrary, concludes from some experiments by R. DE FLEURY that a content of 5% sulphur gives optimum mechanical properties.

For mixtures with different sulphur-content the *form* of stress-strain curves in the same position was found the

same as exactly as could be judged from the determination of slope, or from superimposing the curves obtained on the Schopper machine. Sulphur as a filler does not seem to influence the form of the curve and the figure for slope; for mixtures containing other compounding ingredients stress-strain curves of wholly different forms may be found.

O. DE VRIES and H.J. HELLENDORF, Arch. 2 (1918), 783 and 791; compare J. S. Ch. I. 38 (1919), 93 T and I. R. J. 57 (1919), 1165.

The influence of the sulphur-content on the rate of cure of the mixture is, of course, marked: the higher the sulphur-content, the quicker the mixture vulcanises. Strictly comparative data are, however, still rather scarce; from the available literature it cannot yet be deduced with certainty what the relation is between total sulphur, or non-combined sulphur, and velocity of the reaction between sulphur and rubber.

J. G. FOL and F. C. VAN HEURN (Comm. Delft VI, page 189) determined the combined sulphur when vulcanising mixtures with 2—20% sulphur for a fixed time ($1\frac{1}{2}$ hours at 148°); they found approximately a direct ratio between quantity of added sulphur and combined sulphur.

G. VAN ITERSOM (Comm. Delft VII, page 249) also concludes that an approximate proportionality exists between the coefficient of vulcanisation after a fixed cure ($1\frac{1}{2}$ hours at $3\frac{1}{2}$ atm.) and the amount of total sulphur in the mixture.

O. DE VRIES (Communications of the Central Rubberstation No. 1 (1916), page 20 and 32; compare I. R. J. 52 (1916), 719) found the time of cure necessary to bring the stress-strain curves for a mixture with $7\frac{1}{2}$ % sulphur to a certain position to be 1.5 times as large as with a mixture containing 10% of sulphur; for 6 and $7\frac{1}{2}$ % the ratio was about $1\frac{3}{4}$, for 5 and 6% about $1\frac{1}{6}$ (Arch. 2 (1918), 780).

Some further data on mixtures with $2\frac{1}{2}$, 5 and 10% sulphur are given by C. CHENEVEAU and F. HEIM, Rubb. Ind. 1911, page 335.

From the available data it may be estimated that 0.1 of sulphur above or below our usual amount of 7.5% would cause a difference in rate of cure of about $2-2\frac{1}{2}$ %, or 2—3 minutes in time of cure for ordinary samples of crepe and sheet. Now 0.1 of sulphur, in the usual mixtures containing $92\frac{1}{2}$ to 185 gms of rubber, would mean 0.1 to

0.2 gms, or 1.3 % of the total amount of sulphur; the error of weighing is, of course, never so large, and it will be clear that deviations in the amount of sulphur (errors in weighing, differences in moisture-content of the air-dry sulphur, or loss of sulphur during the mixing operation) can easily be kept so small that they do not appreciably influence the testing results.

From Fig. 23 it might also be concluded that stress-strain curves for mixtures with a higher sulphur-content show a lower coefficient of vulcanisation than those for mixtures with a low sulphur content which have the same form and position. As the curves in Fig. 23 are only schematic, this point needs further investigation; the exact relation, when known, might lead to interesting conclusions.

As regards the influence of different sulphur-contents on the ageing phenomena relatively little is known. In one comparative experiment we found the changes on ageing very much the same for mixtures with 5, $7\frac{1}{2}$ and 10 % of sulphur. The downward movement of the stress-strain curve per day showed approximately the same values, and an increase and subsequent decrease in tensile strength, as described in § 209, was observed in all cases. It is especially interesting to remark that mixtures with 5 % of sulphur, vulcanised till over the maximum of tensile strength (so that the stress-strain curve, after reaching its lowest position, moves upwards again) show on ageing the ordinary downward movement and other changes; but such vulcanisates, on keeping, do not become hard and brittle, but weak and sticky.

See O. DE VRIES and H. J. HELLENDORF, Arch. 4, Nov. 1920.

In comparing different mixtures for testing purposes it will be clear that mixtures with 5 % sulphur and less are not suitable. In the first place the time of cure is very long, and further the fact that a certain stress-strain curve may represent two states of cure complicates the results. The same, to a lesser degree, holds for mixtures with 6 % of sulphur.

Between mixtures with $7\frac{1}{2}$ to 10 % of sulphur there is little to choose. A 10 % mixture vulcanises quicker; but on the other hand the tensile strength falls off much more rapidly

after the maximum has been passed, so that (when a state of cure near that maximum is chosen) a relatively small overcure makes the results of no use. As an advantage of the 10 % mixture it has been advanced that even in prolonged cures, when a coefficient of vulcanisation of 5 % or more has been reached, a sufficient proportion of free sulphur remains to allow the reaction with rubber to go on unhindered, whilst in mixtures with less sulphur the point is earlier approached at which the sulphur is so far used up that the reaction with the rubber is appreciably retarded. From Fig. 20 it will however be seen that in a $7\frac{1}{2}$ % mixture the relation between coefficient of vulcanisation and time of cure is a straight line up to coefficients of 5 or more; in the mechanical changes also we did not note any disturbing influence from this factor in our testing work. On the other hand, the large surplus of sulphur in 10 % mixtures was sometimes supposed to have a bad effect during ageing, but no definite proof of this has as yet been brought forward.

§ 224. Different temperatures of vulcanisation.

In testing raw rubber a constant temperature method is nearly always chosen. It is only sometimes that one finds mention of factory-tests in which different states of cure are obtained by changing the steam-pressure as well as the time of vulcanisation. Whether this method has any advantage in testing the complicated factory mixtures and whether such mixtures show different properties when tested at higher or lower temperatures, is not yet settled. For purposes of comparative testing a constant temperature method is much to be preferred; the results can be more easily compared and interpreted, while the real temperature of vulcanisation need not be exactly determined, as long as no comparison with other methods is desired (compare § 215).

G. D. KRATZ and A. H. FLOWER (I. R. W. 59 (1919), 193), in a mixture containing zinc oxyde and an accelerator, found that the tensile strength is better when not a constant but an increasing temperature of vulcanisation was used, in such a way that the coefficient of vulcanisation showed a constant increase per unit of time of cure.

In how far the temperature of vulcanisation has an influence on the mechanical properties of the rubber, is not yet settled. There is no doubt that heating, in general, has a deteriorating influence; but this influence may be small or negligible during the reconstructing process of vulcanisation, especially when it takes place in moulds, so that the rubber is shut off from air and steam. We have already discussed in § 204 the fact that slower curing rubber has generally a somewhat lower tensile strength than rapid curing types, when tested after our method; and that this difference may probably be ascribed to the longer time they are exposed to the high temperature of vulcanisation. The small difference in tensile strength between matured rubber and smoked sheet, and between the latter and crepe, is probably due to this cause. Another example is furnished by mixtures with only 5 % of sulphur, cured till over the maximum (see § 223): the tensile strength is smaller than for curves in the same position but with a low coefficient of vulcanisation, showing that the vulcanisate by prolonged heating has become not only weaker but also easier to break.

When curing one and the same sample of rubber at different temperatures of vulcanisation, the effect of the higher temperature may be counterbalanced by the shorter time necessary to reach the desired state of cure. The following figures would lead to the conclusion that this is indeed the case; the samples were cured for 90 minutes at our ordinary temperature of 150°.6 C, and for 115 minutes at 148° C:

Sample	Temperature of vulcanisation	Tensile strength	Length at breaking	Length at 1.30 KG	Slope	Coefficient of vulcanisation
I	150.6	1.24	1079	1087	35½	3.60
	148.0	1.27	1069	1073	35	3.72
II	150.6	1.46	1030	1008	34	4.62
	148.0	1.46	1029	1008	33	4.70

Taking into account the fact that in the first case the states of cure were slightly different, the tensile strength is seen to agree very accurately, while the difference in slope is small and would need further corroboration.

A. VAN ROSSEM (in a lecture as yet only published in Dutch) comes to the same conclusion. In experiments in which temperatures from 142° to 164° C were applied VAN ROSSEM found the tensile strength and slope not to be affected by the temperature of vulcanisation.

An argument to the contrary might be derived from the fact that EATON and his co-workers, curing at 140° C, find the tensile strength for crepe much lower than that of smoked sheet (ratio 89 to 100, see § 155, page 336). It might be supposed that the long time of cure (3 1/4 hours) necessary to bring crepe to the desired state of cure, had harmed the tensile strength. This conclusion is however contradicted by the results of SCHIDROWITZ, who uses a temperature of 141° C and finds the tensile strength of crepe to be 95 % of that of smoked sheet, approximately the same figure as from the tests of the Imperial Institute at 148° (95 %) and our tests at 150° (98 1/2 %).

E. SEIDL (G. Ztg. 34 (1920), 797) states, in contradiction of former results of AXELROD, that vulcanisation at a higher temperature gives a stronger product, because vulcanisation is more accelerated by a higher temperature than is the depolymerisation by heat, so that the shorter time, necessary to reach a certain state of cure at higher temperatures, more than compensates for the effect of the heat.

From the experiments by K. GOTTLÖB (G. Ztg. 30 (1916), 303) SEIDL concludes that, when using a fixed temperature of vulcanisation, a more rapid cure (for instance by using an accelerator) gives a higher tensile strength of the vulcanisate.

On the contrary, P. BREUIL (C. Gp. 1906, page 558) concluded from some experiments by R. DE FLEURY that an increase in temperature causes a much greater deterioration in resistance and distensibility than a longer time of cure at a lower temperature, and holds 140° C to be the optimum temperature.

The velocity with which vulcanisation proceeds increases markedly with higher temperatures. For each increase of 1° C (1° 8 F) the velocity increases by about 10 %, and for a difference of 10° C it increases 2.4 to 2.7 times.

P. BREUIL (C. Gp. 1911, page 5300) mentions a temperature-coefficient of 4 for Para-rubber between 135 and 145° C.

D. SPENCE and J. YOUNG (Z. Koll. 11 (1912), 28) found the temperature-coefficient (increase in velocity for 10° C increase in temperature) to be 2.67 between 135 and 155° C for mixtures with 10 % of sulphur.

O. DE VRIES (Communications of the Central Rubberstation No. 1 (1916), page 14 and 31; compare I. R. J. 52 (1916), 719) found that to obtain the same position of the stress-strain curve the time of cure at 140° C had to be taken very nearly double that at 148° C, when using mixtures with 5–10 % of sulphur. This means a temperature-coefficient of 2.4.

J. G. FOL and F. C. VAN HEURN (Comm. Delft VI, page 187) in experiments with mixtures containing 7½ % of sulphur, found coefficients of about 2 and about 2.4.

G. D. KRATZ and A. H. FLOWER (I. R. W. 59 (1919), 194) assume a temperature-coefficient of 2.5 (rate of cure increasing with 50 % from 290 to 298° F). See also G. D. KRATZ, I. R. J. 51 (1916), 661.

A. VAN ROSSEM (in a lecture as yet only published in Dutch) for mixtures with 7½ % sulphur found coefficients from 2.57 to 2.72.

D. F. TWISS and S. A. BRAZIER (J. S. Ch. I. 39 (1920), 125 T) for a mixture with 10 % sulphur found a coefficient of 2.3 for temperatures of 128–168° C.

A coefficient of 2.3 (doubling of the rate of cure for each 15° F) is assumed in the calculation of a table for the relation between pressure and time of cure, published in I. R. J. 59 (1920), 653.

A. O. BOURN (Rubb. Ind. 1914, 413; also I. R. J. 45 (1913), 120), using a mixture containing litharge and whiting, found the time of cure to be doubled for each decrease in temperature of 11° F between 194 and 304°. This means a temperature-coefficient of 3.2 for 10° C. For temperatures above 304° a coefficient of about 1.6 was observed. BOURN connects this difference with the change in liquid sulphur above 304° F.

From the example in the table on page 542 a ratio of 1.28 is calculated for a difference of 2° 6 C, or a temperature-coefficient of 2.6. In § 215 we mentioned that a deviation of 0° 1 C in our temperature of vulcanisation causes a difference of ¾–1 % in time of cure or coefficient of vulcanisation, from which a temperature-coefficient of roughly 2.4 (2.06–2.69) is calculated for a difference of 10°.

Whether the temperature of vulcanisation has an influence on the slope of the stress-strain curve or on the ageing properties of the vulcanisate is not yet known.

G. D. KRATZ (I. R. J. 51 (1916), 662) found temperatures from 137° to 162° C without influence on the keeping properties (influence of air, sunlight and time of keeping) in a vulcanisate containing zinc oxyde.

In the choice of a temperature for vulcanisation, higher temperatures have the advantage that the test is sooner finished, and more vulcanisations can be made on one day. Moreover, as the control of the thermometer or pressure gauge is rather tedious work, the chance is great that at the end of long vulcanisations, say of 3 or 4 hours duration, the constant attention to the adjustment of the steam flow will slacken somewhat. A supposed drawback, viz. that the properties of the rubber are injured by the higher temperature, seems to be compensated by the shorter time of cure, as we have discussed above; another argument that is sometimes heard, viz. that small deviations and errors in temperature will have a larger influence on the results when high temperatures are used, is erroneous, as 1° difference in temperature causes 10% difference in rate of cure at higher as well as at lower temperatures or, in other words, as the larger influence of deviations in temperature is balanced by the shorter time of cure at higher temperatures.

B. J. EATON (Agric. Bull. F. M. S. 5 (1916), 60) prefers a lower temperature such as 140° , because the time of cure is longer and the margin of error in respect to time (duration of vulcanisation) is larger.

When using a mixture with $7\frac{1}{2}\%$ sulphur a rather high temperature of vulcanisation is to be recommended, so as to reduce the ordinary time of cure to about $1\frac{1}{2}$ —2 hours, which is convenient to work with, i.e. not so long that it retards the progress of the work, and at the same time long enough to make small deviations in the closing and opening of the pan etc. negligible. For mixtures with 10% of sulphur, which cure quicker, a lower temperature can eventually be used.

In the investigations on raw rubber with rubber-sulphur mixtures, running on the lines described in this book, the following combinations of temperature of vulcanisation and sulphur-content of the mixture are amongst those found in literature:

	Steam pressure	Temp. Celsius	Sulphur on mixture	Sulphur on rubber	
Governm. Inst. Delft (Holland)	52 lbs	148°.25	7.5	8.11	Comm. Delft V, page 137.
Ph. Schidrowitz c. s.	40 lbs	141°	7.41	8.0	I. R. J. 51 (1916), 505 and 751; <i>ibid.</i> 52 (1916), 615.
Imperial Institute (London)	50 lbs	147°.6	10.0	11.11	Bull. Imp. Inst. 14 (1916), 499.
B. J. Eaton c. s. (Dept. of Agriculture, Kuala Lumpur)	—	140°	10.0	11.11	Bull. F. M. S. No. 27 (1918), 27 and 30.
H. P. Stevens (London)	35 lbs	138°	10.0	11.11	Bull. R. G. A. I (1919), No. 1, page 37.
Central Rubber-station, Buitenzorg	61 lbs = 43 KG per cm ²	150°.6	7.5	8.11	Chapter XVII and XVIII of this book; compare I. R. J. 52 (1916), 717 and <i>ibid.</i> 53 (1917), 101.

§ 225. Standard time of cure methods.

Once the sulphur-content of the mixture and the temperature of vulcanisation fixed, the further testing can be conducted in different ways. Either a fixed time of cure, or a fixed state of cure can be adhered to; and in each case different standards may be chosen.

Using a standard time of cure gives the simplest and easiest method of testing. All samples are treated in exactly the same way during all operations; they are not only mixed with the same proportion of sulphur but also cured side by side. One has not to wait till sufficient samples for a certain time of cure have accumulated, or else fill the vulcaniser with too small a number of samples: all samples that await testing can be put together in one charge of the vulcaniser. Moreover the results are very strictly comparable also in this respect that the heating and cooling periods at the beginning and the end of each vulcanisation form always exactly the same part of the total heating.

On the other hand the data that may be derived from tests at a standard time of cure are so much less than when using a standard state of cure that the latter method, though more complicated, is to be preferred in nearly all cases. The fixed time of cure brings the samples to different states of cure, according to the rate of cure of the rubber in question. A slow curing rubber will reach only a very low coefficient of vulcanisation and show a stress-strain curve going straight upwards and lying very much to the right in Figs. 14 and 18; a rapid curing rubber will reach a high coefficient, show the maximum of tensile strength or even surpass it and eventually be quite brittle. Of course, when arranging a testing method with a fixed time of cure, the time of cure is so chosen that it brings the bulk of plantation-rubber to an intermediate state of cure, while rapid curing samples are not too far over-vulcanised; but even then the extreme samples are brought to very divergent states of cure.

From such tests the rate of cure of the samples can be determined very well by the coefficient of vulcanisation or by the position of the stress-strain curve. Even without using a stretching machine, by simply subjecting a small piece of the sample to the standard cure and determining its coefficient of vulcanisation (for which 1 gm of vulcanisate is sufficient), a very exact comparison of rates of cure can be obtained. When using the mechanical properties, the load at a certain length (for instance 800 or 850 % elongation) is best suited for comparison, and the rates of cure may be expressed in this way; it must then, however, be borne in mind that there is no direct proportionality between rate of cure and load at a certain length.

When the relation between coefficient of vulcanisation and position of the stress-strain curve (i. e. whether for a certain curve the coefficient shows a higher or a lower value than the average) is in the future eventually found to have any importance in testing (compare § 206), then on this point conclusions may also be drawn from standard time of cure tests.

The other properties mentioned in this book can however not be determined by the standard time of cure method. For the slope this is clear without much further discussion:

the slope is not the same in different states of cure (see § 221), and its determination would be wholly impossible for samples with a low rate of cure or for quick curing samples which become over-vulcanised and brittle, as in such cases the stress-strain curve does not extend to its characteristic upper part where slope is determined.

A breaking point is, of course, reached for each curve also in standard time of cure testing, and with the exception of over-vulcanised, brittle samples this might give indications as to the tensile strength: the further advanced the breaking point on a certain curve, the higher the tensile strength. To connect and compare such data for samples with different rates of cure would however only be possible when the average curve of breaking points is known, so that a certain breaking point might be compared with the average breaking point for that position of the stress-strain curve (state of cure); and even then a complicated manner of expression would be necessary, owing to the fact that the upper parts of the stress-strain curves show different inclinations. A difference in breaking load of 0.1 KG would, as it is measured horizontally, mean a much larger difference in real tensile strength for slow curing, under-vulcanised samples than for rapid curing, much further vulcanised ones.

Moreover, as we saw in Fig. 18, the curves for breaking points do not coincide for all samples, but differ in position according to slope. Average curves of breaking points would therefore have to be established for a number of types of rubber with different figures for slopes.

The Government Institute at Delft tested a large number of samples after the standard time of cure method, taking a fixed cure of $1\frac{1}{2}$ hours at $148^{\circ}.25$ C (52 lbs) and using a mixture of $92\frac{1}{2}$ rubber and $7\frac{1}{2}$ sulphur. An average curve of breaking points was derived by A. VAN ROSSEM from the material so obtained (Comm. Delft V, page 156) which, as it was calculated for crepe and smoked sheet, may be taken to hold good for slopes of 34—38, on the average 36. Of course such a curve of breaking points is not strictly comparable with those in Figs. 14 and 18: the latter hold good for one sample of rubber, cured for different times, while in the curve constructed by VAN ROSSEM the left part has been procured by the quick curing samples, the right part by the slow curing ones. Had these

slow vulcanising samples been cured to the maximum tensile strength, then they would probably have given a somewhat lower figure for tensile strength than the rapid curing ones (compare § 204) and a curve would have been obtained lying somewhat to the inside (to the right) of the maximum found by VAN ROSSEM.

For permanent set and other properties which change with increasing state of cure, the same reasoning holds good: a strict comparison of different samples would only be possible if average curves were known for the decrease of permanent set with increasing state of cure, which curves would then have to serve as a basis of comparison.

To sum up: the standard time of cure method is simple and easy in the execution and gives good results when only rate of cure and uniformity on this point have to be judged. The figures for tensile strength are difficult to interpret and give an uncertain comparison, whilst slope cannot be determined by this method. Though easy, it does therefore not give sufficient data to judge and compare different types of plantation-rubber.

In special cases a comparison of samples vulcanised together in one cure may have advantages. We gave examples of this in Figs. 5 and 6, where samples from one estate were cured together: the degree of uniformity is illustrated clearly in this way. Also, when a very exact comparison between samples with a relatively small difference in rate of cure is desired, these may be cured side by side so that errors in vulcanisation have the same influence for all samples and differences in rate of cure are found without applying corrections or without uncertainties as to experimental errors in vulcanisation.

Strictly speaking, most of the methods of testing said to follow a standard or correct state of cure method are a compromise. For actual testing it would be impossible always to give the desired cure exactly to the minute and second. Fixed intervals are mostly chosen, sometimes of 15 minutes, sometimes (as in our testing) of 5 minutes, and the exact time of cure is estimated from these approximate cures.

Our method of testing might be described as a „standard time of cure method, using some 12 or 30 different standard times, with intervals of 5 minutes (from 75 to 130 for ordinary samples, from 30 to 180 or more for special cases)“.

To combine the advantages of the standard state of cure methods with the quickness of the standard time of cure, a simple combination, using for instance 3 or 6 standard times of cure, might perhaps give useful results in certain cases. As mentioned in § 200 (page 464) a cure differing 5 minutes or even more from the standard is sometimes regarded as sufficient in our testing work, when quick results are of more importance than the highest degree of accuracy. The tensile strength, time of cure and slope for standard state of cure may be estimated with sufficient accuracy from the results of such approximate cures.

§ 226. Standard state of cure methods.

The mechanical properties of different samples are best compared by bringing the vulcanisates to the same state of cure. This may be either some „optimum“ or „correct“ state of cure, which we will discuss in the next paragraph; or any arbitrary standard state of cure which gives a good basis for comparison.

The necessity of bringing the samples to a strictly comparable state of cure, in order to eliminate the differences caused by rate of cure, was especially put in the foreground by PH. SCHIDROWITZ (see, for instance, *Rubb. Ind.* 1914, page 212; *Rubb. Rec.* 1914, page 373).

The standard state of cure may be determined by:

- a) a certain coefficient of vulcanisation.
- b) certain mechanical properties, for instance a certain position of the stress-strain curve.

One of the principal arguments for using the coefficient of vulcanisation as a basis is that theoretically the chemical status of the vulcanisate, the degree to which rubber and sulphur have united, constitutes a more fundamental property and is a more reliable gauge of the state of cure than the mechanical properties, which change by ageing, temperature etc.

On the other hand the buyer does not judge rubber goods upon their coefficient of vulcanisation, but upon their mechanical properties, which alone are of practical importance.

Of course, when one wants to gain as complete an insight as possible into the properties of so complicated a substance as vulcanised rubber, both coefficient of vulcanisation and mechanical properties have to be taken into consideration (compare § 206).

Standard coefficient of vulcanisation.

When using a method of testing based on this principle, the sample is first subjected to a trial vulcanisation by adding a piece of the mixture to any charge of the vulcaniser that will be cured for a suitable time. The coefficient of vulcanisation is determined in the vulcanisate, and as the coefficient increases in direct ratio with the time of cure (compare § 206), the time necessary to produce a vulcanisate with the desired standard coefficient can be calculated with sufficient accuracy. A second vulcanisation for that time of cure is then effected, and the coefficient and mechanical properties are determined. When the coefficient still differs somewhat from the standard, the time of cure and the mechanical properties have to be reduced to the values for standard state of cure by applying corrections. This means that the increase of tensile strength with increasing coefficient of vulcanisation must be known; the relation is generally assumed to be rectilinear, at least for not too high coefficients and not too large deviations, but figures and correction-tables have not yet been published.

Of course, different values for the coefficient of vulcanisation may be chosen as standard; a figure between 2 and 3 is preferred by some, as it represents the technical state of cure to which most rubber articles have to be brought, and therefore gives the most strict comparison with factory results.

A drawback of this method is, that the determination of the coefficient of vulcanisation takes several days. The duration of the extraction with acetone varies from 1 to 7 days in different prescriptions; the destruction of the rubber

and the sulphur determination as sulphate take at least two days. As these operations have to be done at least twice to obtain the definite figures (once for the trial, once for the final test), it takes rather a long time before the testing results are to hand.

H. P. STEVENS in his researches uses a standard coefficient method, in which a coefficient of vulcanisation of 3.0 is chosen (Bull. R. G. A. 1 No. 1 (1919), page 37). The relation between the load at 9 or 10 times the original length and the coefficient of vulcanisation is depicted for some examples in J. S. Ch. I. 37 (1918), 283 T; the curves for the relation between breaking load (tensile strength) and coefficient of vulcanisation, from which the corrections in the former property are derived, have not yet been published.

Standard mechanical properties.

In this method a certain position of the stress-strain curve, i.e. a certain relation between load and elongation, is mostly chosen as standard. A trial vulcanisation must produce a preliminary insight into the rate of cure and the time necessary to reach the standard; a final vulcanisation produces a stress-strain curve sufficiently near to the standard. This method is quicker than the former one, as the mechanical properties may be determined on the day after vulcanisation, so that trial and final vulcanisation may be finished within a few days; the method is simpler, because the rather tedious sulphur determinations are avoided; but though it may give excellent and strictly comparable results in one institute, it is probably not so suited as a basis of comparison between different institutes, when temperature of testing room, climate, type of testing machine and so many other factors vary.

The method may be so executed that a standard curve is drawn on a piece of paper, and the curves obtained on the testing machine are directly compared with this standard curve by superimposing the papers one on the other in the right position and holding them to the light. One may also determine or calculate the length at a certain load (see § 220), or the load at a certain length, and compare the figures so obtained with the standard ones. The latter method has the advantage that the average of several

determinations (several rings from one vulcanisate) can be used at once, so that the determination of their average deviation from the standard curve only takes one operation.

As the form of the stress-strain curve is not the same for different types of rubber, but shows differences which we discussed in § 200, 202 and 221, and which find an expression in the figure for slope, it is, strictly, not correct to speak of and use a standard curve: the curves for different types of rubber do not accurately coincide, though the differences may be so small that they are overlooked in not too exact testing, and partly disappear amongst the irregularities, oscillations etc. of the stress-strain curve, especially when the testing machine is somewhat worn.

As described in § 200, we use in our testing a „standard point” method, in which the standard state of cure is so chosen that the curves all pass through one point, for which the length at a load of 1.30 KG is 990 % (elongation 890 %). The arguments for choosing this standard have been set forth in § 200 and 205. The argument heard against the choice of this standard, viz. that the rubber is technically over-cured, is of no importance for comparative tests; the fact that a real over-cure, resulting in brittleness, is sooner reached, might even be an advantage in testing, as it shortens the ageing tests.

Of course, other standard curves may also be chosen, and a curve giving vulcanisates with a coefficient of approximately 3, representing the ordinary technical cure, might also serve the purpose if the property called „slope” can be derived from it as easily as from curves for further advanced cures.

A standard curve method has also been adopted by B. J. EATON and his co-workers (Bull. F. M. S. No. 27 (1918), 46) who, however, use an optimum cure method at the same time (see § 227). Figures determining the position of this standard stress-strain curve have not yet been published; from diagram 4 in Bull. F. M. S. No. 27 (1918), page 47, a length at 1.30 KG of appr. 985 %, and a load at 850 % length of appr. 1.1 KG may be estimated for EATON's standard curve, while the coefficient of vulcanisation is 4.3—4.9 (mixture 90 rubber and 10 sulphur, temperature of vulcanisation 140° C).

In the method of testing described in this paragraph it is the time of cure that is varied so as to obtain the standard state of cure, and rate of cure is determined in the form of „time necessary to reach the standard state of cure”. Another issue (which, however, as far as we know, has not yet been worked out systematically) would be to add an accelerator — be it one of the common technical accelerators, or the natural accelerator in some form or other — in such an amount that the standard state of cure is reached in a fixed time. The rate of cure would then be measured as the inverse of the amount of accelerator added. This method would combine the advantage in operating obtained with a standard time of cure (see § 225) with the more valuable and better comparable results obtained from a standard state of cure; but whether it is practicable, and what form it would have to take, remains to be seen.

§ 227. Correct or optimum state of cure methods.

The idea of bringing the rubber to some optimum state of cure, so that it may show its best in the tests, has a certain fascination; examining the vulcanisate in different states of cure, so as to pick out the best, has been advocated by several authors.

See for instance D. SPENCE and W. F. RUSSELL, Z. Koll, 13 (1911), 43; PH. SCHIDROWITZ, Rubb. Ind. 1914, page 213, and others.

Under this head the following methods may be enumerated :

- a) maximum tensile strength;
- b) maximum product of load and elongation;
- c) theoretical correct cures.

Perhaps the *maximum of tensile strength*, which we described in § 205, may have a theoretical interest as a state of comparableness for different samples; the relation of the elongation at which the maximal tensile strength is reached with slope (see § 205) points in this direction.

In practical testing however the maximum of tensile strength is of no use, as the number of observations necessary to determine it, even with a very moderate degree

of exactness, would be far too large. In special cases, for instance an elaborate comparison between Brazilian and plantation methods of preparation, it may be of importance to investigate the whole range of cures and determine the maximum of tensile strength accurately; but as this involves a series of vulcanisations for increasing times of cure, and the testing of several tens or even several hundreds of rings, such an elaborate comparison cannot be used as the base of regular testing, for which a simpler and quicker method must be chosen.

After what has been said in § 205 and 226 it will be superfluous to repeat that, though our standard state of cure is intentionally chosen at the maximum tensile strength for ordinary crepe and smoked sheet, samples with a high figure for slope are not brought to the maximum of tensile strength in our testing, and may show somewhat higher figures for tensile strength when vulcanised further than to our standard state of cure.

The same very considerable amount of determinations would be involved when the *maximum of the product of load and elongation* is chosen as a base of comparison. A series of successive cures have to be made, and the breaking load for each cure has to be determined with sufficient accuracy (that is, using a rather large number of rings), so that this method also is unfit for practical, quick, comparative testing.

The product of load and elongation is an expression for the „work done” during the stretching operation, and as such has a certain theoretical importance. Whether its maximum, which lies somewhat higher on the paper than the maximum of tensile strength (i. e. at a somewhat greater elongation, but a somewhat smaller tensile strength), has any special theoretical or practical significance, has not yet been established.

B. J. EATON bases his tests, besides on a comparison after the standard curve method (see § 226, page 553), also on the maximum product. The maximum product of load and elongation generally lies somewhat lower on the paper (is reached in a somewhat longer time) than EATON's standard curve. For each of the different states of cure above and below

the maximum, which are tried in the comparison, slabs of two rings are made and the figures for the better of the two rings are taken. (Bull. F. M. S. No. 27 (1918), page 45). Of course, figures for the breaking point of only one ring are subject to a considerable experimental error, and it seems doubtful whether any great degree of accuracy can be reached in determining the maximum product, when using only such a relatively small number of observations. The figures both for „maximum product” and „standard curve” are given side by side in EATON’s publications; any advantage in the „maximum product” over the standard curve figures does not appear, and the adoption of only the latter would allow of concentrating all the rings in one final test and so obtaining more figures to determine the average tensile strength.

A *theoretical correct or optimum cure*, which constitutes a state of real comparableness of the inner status and properties of different types of rubber, would be the ideal base for comparison, provided that the number of tests necessary to determine it remains within reasonable limits. Such a method has been worked out by PH. SCHIDROWITZ, H. A. GOLDSBROUGH and E. HATSCHEK. The stress-strain curves are assumed to be conchoidal curves, while the upper, straight parts of the curves for successive cures are supposed to run parallel. From this a state of cure is derived in which the parameters of the conchoidal curve are equal, thus representing an ideal balance between toughness or tenacity and limit of extension.

PH. SCHIDROWITZ, H. A. GOLDSBROUGH and E. HATSCHEK, J. S. Ch. I. 38 (1919), 347 T; see further PH. SCHIDROWITZ, Rubb. Ind. 1914, page 212.

In applying this method a trial vulcanisation is first made to learn the rate of cure of the sample, and at the same time the slope of its stress-strain curve. From the theoretical deductions referred to above a close relationship is deduced between the slope and the position of the stress-strain curve giving optimum cure, viz.:

Slope	33	35	37	39	41	43	45
Length of optimum curve at 1.04 KG.	1008	992	975	959	942	925	909

From the slope found in the preliminary cure the position of the optimum curve for the sample in question is deduced

by the use of the above table, and at the same time it can be estimated how much the time used in the preliminary cure must be altered to reach that optimum state of cure. The course of testing and the work involved are therefore the same as in the standard state of cure methods described in § 226, and the method is just as practicable. It has however not yet been shown in how far this optimum state of cure actually gives a better base for comparison than the standard states of cure used in other methods of testing.

The data published by SCHIDROWITZ and co-workers to prove their theory are rather scarce, and an elaborate experimental material for comparing this method with others has not yet been made available. We found that two of the principal assumptions do not strictly hold good in our testing; the upper straight parts of different stress-strain curves for one sample are not parallel, and the slope is not a constant for different states of cure (see § 221). On the other hand a very near parallelism was found to exist between the position of the maximum of tensile strength and the optimum cure of SCHIDROWITZ c. s. (see § 205), which seems to indicate that the theoretical speculations of these authors are substantially correct, though perhaps built up on too elementary assumptions.

Though the „optimum cure” method as worked out by SCHIDROWITZ c. s. is therefore just as practicable as the standard state of cure methods treated in § 226, proof of its superiority is still lacking, and further data will have to be awaited before its advantages and disadvantages can be fully judged.

§ 228. Comparison and standardisation of testing methods.

The methods now in use for testing raw plantation-rubber, of which some have been reviewed on page 546, differ not only in the main factors treated in this chapter, viz. percentage of sulphur, temperature of vulcanisation, and interpretation of results, but also in many minor points, such as form and dimensions of test piece, type of testing machine etc. An elaborate comparison between the results obtained in different institutes, based on an exchange of samples, is not yet available; from the data hitherto published some general conclusions may however be drawn.

Average figures for relatively large numbers of samples of smoked sheet and crepe have been mentioned in § 155; taking the figure for smoked sheet as 100, the results for crepe may be summarised as follows:

	Ratio for tensile strength	Ratio for time of cure
SCHIDROWITZ c. s.	95	117
Imperial Institute	95	121
EATON c. s.	89	118
Central Rubberstation. . . .	98 $\frac{1}{2}$	120

The figures for tensile strength agree very well, with the exception of the lower results obtained by EATON c. s. (see the discussion in § 224, page 543). The figures for time of cure show a very satisfactory agreement, especially when it is taken into account that the methods of preparation may have varied to a not unimportant degree. On the whole a decided parallelism in the figures both for tensile strength and time of cure is apparent from this summary.

For matured rubber, as compared with crepe or smoked sheet, the following figures may be compiled from § 108:

	Ratio for tensile strength	Ratio for time of cure
EATON c. s.	103 $\frac{1}{2}$	220
H. P. STEVENS	—	171
Central Rubberstation	102	159—238

These figures, of course, are far less comparable than the above, as maturation may have proceeded more or less (for instance owing to differences in the amount of acetic acid used in coagulation etc.). Still the increase in rate of cure found by different methods is of the same order of magnitude.

For slope, on which property data have only been published by SCHIDROWITZ c.s. and ourselves, comparable figures are still scarce. As the average for a large number of crepes and smoked sheets, SCHIDROWITZ and GOLDSBROUGH found 35.5 and 36.2 respectively (see page 336), whilst our average figures are 35.8 and 36.7 (§ 155), in very good agreement. For ordinary brown crepe from the same estates the former authors found average figures from $37\frac{3}{4}$ to 39, which figures are quite common in our testing (compare Chapter XIII and § 202). A closer comparison, executed in the same or similar samples, is still lacking.

A *standardisation of methods of testing* has already been advocated long ago, and at the London Rubber Exhibition of 1908 a Committee was formed to study this question.

See Lectures 1908, page 283; Rubb. Ind. 1911, page 393.

Little has transpired of practical results, and it may be assumed that the difficulties were found too great. These difficulties are indeed considerable. In the first place the real, scientific knowledge of rubber and rubber testing was much too small and is still scarce sufficient to form a solid base for methods of testing to be adopted by all. In the second place the influence, the advantages and the disadvantages of different minor points, such as form of test piece and testing machine, room temperature etc, are insufficiently known. In the third place a standardisation is always difficult to attain, because nobody is inclined to change his method of testing and give up the strict comparability of new with old results unless the new method is so soundly established that further changes of method need not be expected. To these general arguments come further factors, such as the delicate question that preference must be given to one type of testing machine or vulcaniser, to the exclusion of others, without favouring any particular firm etc.

Strict standardisation, so that the same method is followed in, and exactly the same figures are obtained by, all institutes will always be difficult to attain. In the mean time the results might be made more comparable by expressing them not as the absolute values found, but according to a relative scale.

H. P. STEVENS (Bull. R. G. A. 1 No. 1 (1919), page 38) proposed to express rate of cure on a percentage basis, taking as 100 the average rate of cure of smoked sheet and crepe. To make this proposition suitable for general use it would be necessary to establish and fix a generally adopted and easily accessible average value to be taken as standard (100). Further it has still to be proved whether a percentage basis is the correct one for comparison: it remains to be investigated whether the time of heating and cooling — which, of course, forms a larger part of the total heating in short cures than in long ones — does not form a disturbing factor, having a larger or smaller influence in one case or the other.

Something might decidedly be reached when one institute, which keeps to very rigidly standardised methods, made available for comparison samples of rubber representing for instance the values 50, 100 and 150 on a comparative scale. Each institute, by testing these standard samples on its own lines, might then compare its actual figures with the comparative scale and recalculate its results on this basis.

§ 229. Mixtures with other components.

Rubber testing is, of course, far from exhausted when using only a rubber-sulphur mixture. This mixture is very well adapted to bring to light the properties of raw rubber, and especially to show clearly the differences in its rate of cure; and as such it is probably the best one for the study of methods of preparation. For technical purposes the aim is not to bring out the properties and eventual differences of different types of rubber as distinctly as possible; the question to be answered is: can a certain rubber be used in a certain mixture for a certain purpose, or can a mixture be found that gives satisfactory results with a certain rubber.

A considerable amount of testing work has already been published in which technical mixtures and artificial accelerators were used; but a complete systematic study of the influence even of the most common compounding ingredients is still lacking. Data on the influence of increasing amounts of lead oxyde, zinc oxyde and such fillers, when added to various rubber-sulphur mixtures, would be of as much importance for a general knowledge of vulcanised rubber as a study of the effect of increasing

amounts of different accelerators on the principle types of technical mixtures. A large field for systematic research (or for publication of results which are of general interest) still lies open.

We will not give a review of what has already been done and published in this field, as so little is yet known about the relation to preparation and properties of the raw rubber. Even the influence of different compounds, on the properties treated in this book (tensile strength, slope, rate of cure) is as yet only imperfectly known.

One of the points that has been discussed at some length is whether the natural accelerator in rubber (especially in matured rubber) has the same pronounced effect in mixtures containing other substances than rubber and sulphur alone. In several such mixtures the accelerating effect was still very noticeable, but in others, containing for instance lead oxyde or artificial accelerators, the differences caused by the natural accelerator wholly or practically disappeared.

See for instance B. J. EATON and J. GRANTHAM, J. S. Ch. I. 35 (1916), 1048, further Bull. F. M. S. No. 27 (1918), 113; H. P. STEVENS, J. S. Ch. I. 35 (1916), 1142.

This means that the differences in rate of cure found when testing a rubber-sulphur mixture are in many cases of no practical importance, or at least can be easily levelled up by the manufacturer. Whether it is cheaper to regulate the amount of natural accelerator in the preparation on estates, or to add some accelerator or other compound that counteracts its effect later on, remains to be seen; and whether for special purposes a rubber of guaranteed uniformity and good inner properties would have a higher value for the manufacturer, is also still unsettled. It might be considered as the task of research chemists on the manufacturing side to investigate such questions and formulate the wishes of manufacturers; the chemist on the plantation side has to investigate the causes of deviations or defects, and to formulate the possibilities in rubber preparation, the properties and the uniformity that can be and are obtained either in actual practice or when special care and well standardised methods

are applied. The present state of affairs, seen from the latter standpoint, has been sketched in the foregoing pages; further progress in this direction might be much stimulated by the publication of research from the manufacturing side.

CHAPTER XX.

PHYSICAL PROPERTIES AND TESTING OF UNVULCANISED RUBBER.

§ 230. Mechanical properties and testing of raw rubber.

Raw rubber has to a certain degree similar properties, as regards distensibility, elasticity etc, to those to be expected in the manufactured product; and though raw rubber is never used as such, but has to undergo more or less integral changes such as dissolving or vulcanisation, the idea that the elasticity and strength of the raw rubber bear a direct relationship to its properties after manufacture presents itself very readily. We discussed the structure of the coagulum and the total reconstruction during vulcanisation in § 105, and stated that the mechanical properties of the raw rubber are destroyed and rebuilt for the greater part, if not wholly, during vulcanisation, so that they are in the first place of importance for the preliminary stages of manufacture such as dissolving, masticating and mixing. Still, these manipulations are important enough to warrant a study of such properties of rubber as determine its behaviour in this respect; moreover, the structure or state of gelatination of the rubber forms an interesting point in the study of methods of coagulation and preparation.

While the value of hand pulling and of tooth and nail tests on raw rubber is dubious and their result often delusive, mechanical and other tests on raw rubber may have a certain importance and perhaps deserve more attention than is usually given to them.

Unfortunately the market product is not in a suitable form for mechanical testing. The irregular granular structure of crepe, with its many small holes, and the ribs on smoked sheet — to say nothing of the rather large differences in

thickness even in one and the same piece—practically forbid mechanical tests, because the experimental error far exceeds the differences which are to be expected between different types of rubber. For experimental purposes plain sheets might purposely be prepared, from which rings or strips can be cut. The use of another type than the Schopper stretching machine would then impose itself, as the latter with raw rubber produces very steep and upright curves, the breaking load being some 0.02—0.05 KG per mm^2 for an elongation of 500—800 %. It is however not easy to prepare plain sheets of a standard thickness, as every factor in preparation which affects the hardness of the coagulum has an influence on the thickness after rolling. Even if the freshly rolled, wet sheets are of even thickness, then the air-dry product may show differences, as the contraction during drying depends upon the moisture-content and other factors.

Bringing the rubber by some means or other into the desired form for mechanical tests generally means destroying its original status; mechanical tests on raw rubber have, for these reasons, not gained much importance either in relation to preparation on estates, or to manufacturing processes.

Extensive and interesting studies on the physical and mechanical properties of raw rubber and the application of the theory of elasticity have been made by H. BOUASSE (C. Gp. 1904, No. 6 en 7; *ibid.* 1906, pages 398, 430, 457 and 473; *ibid.* 1912, pages 6211 and 6291). These methods have not yet been investigated as to their importance for manufacturing processes, nor have differences in methods of preparation of raw rubber been studied on these lines.

CL. BEADLE and H. P. STEVENS (I. R. J. 35 (1908), 26) showed by tests on differently treated pieces from the same block or biscuit how absolutely futile are tests on raw rubber, unless the samples are treated in identically the same manner. They gave figures for the influence of method of drying, pressure, freezing and heating which prove the large influence of these procedures on raw rubber (tensile strength, stretch and specific gravity).

The same authors (I. R. J. 35 (1908), 184) suggest a uniform method of preparation of test pieces comparable with the manufacture of cut sheet; they however much prefer testing after vulcanisation.

V. HENRI (Le Latex (1908), page 379; also C. Gp. 1920, page 10197) made tests on strips of raw rubber of a square cross-section of 3 by 3 mm, and found a rubber coagulated by the aid of sulphuric acid and phenol (see § 86) to be especially elastic and strong in such tests; the raw rubber showed a breaking strain of 0.16 KG. per mm² and an elongation of 545 %.

The experiments of F. C. VAN HEURN (Comm. Delft I, page 35 and III, page 106) clearly demonstrate the large error of determination when testing raw rubber.

As to the influence of the composition of the latex on the mechanical properties of the raw rubber data are very scarce. The fact that very young trees, too young to be tapped, produce a rubber that is brittle on hand pulling, was mentioned in § 24; such rubber also shows a low viscosity and a low tensile strength after vulcanisation. In actual practice a „shortness” or brittleness in sheet-rubber is also sometimes noted; such sheets mostly show a somewhat low viscosity but a normal tensile strength after vulcanisation. Whether this deficiency is also connected with the age of the trees is not wholly cleared up; the defect may be mostly or always brought in connection with young divisions newly taken into tapping, but neither trees of a certain age (say 4 or 5 years), nor trees taken for the first time into tapping always show this brittleness. However it is probably not the real, but the physiological age of the tree, and perhaps other circumstances also, which determine such properties.

Methods of coagulation may have a considerable influence on the properties of the raw rubber. We mentioned in § 88 the astringent action of alum, which produces a very tough sheet; in § 105 some further examples were given. The subject has, however, not yet been followed up in a systematic way, as methods of testing which may give the desired information have not yet been sufficiently developed. As we discussed in § 105, these points deserve full attention in relation to processes such as mastication, breaking down on the mills, mixing with compounds, use in solutions or cements etc.; but manufacturers have not yet made clear what are the properties they desire in one case or the other, and what tests have to be applied.

The effect of different methods of coagulation and drying, not only on the structure of the coagulum but also on the mechanical properties of the raw rubber, was especially studied by V. HENRI (Le Latex, page 354 and 447, compare also § 105) who found the breaking load and elongation of strips of raw rubber, coagulated by different methods, to vary largely.

Other factors in preparation may also have an influence on the mechanical properties of the raw product. Heat, for instance, weakens the rubber; and also when cooled down after having been heated to high temperatures, the mechanical properties of the raw product remain altered, the elongation reached by a certain load being greater, and the rubber therefore weaker.

On the general effect of heat on raw rubber see for instance A. SCHWARTZ and PH. KEMP, C. Gp. 1911, page 5293.

V. HENRI (Le Latex, page 385; also C. Gp. 1920, page 10198) found in a special case (rubber coagulated with sulphuric acid and phenol, see above) that heating the unvulcanised rubber for 20 minutes at 100° C did not alter the tensile strength, but increased the elongation at a certain load and the deformation markedly (when testing the raw rubber). Heating for four hours at 110° C made the rubber quite sticky.

F. C. VAN HEURN (Comm. Delft III, page 98) found the tensile strength of raw rubber to decrease by heating at 120—140° C in carbon dioxide or at 100° in the air, but to increase by 10 hours heating at 100° in carbon dioxide.

§ 231. Swelling and solubility.

As mechanical tests on raw rubber present the difficulties just described, which are principally related to its irregular form, other means have been sought to get an insight into the structure of rubber in the raw state. One of the most promising is, perhaps, swelling the rubber in different fluids or in their vapours. Raw rubber takes up a considerable amount of organic solvents without losing its coherence; and the velocity with which these substances are absorbed, the changes in the swollen product etc. may probably give valuable indications as to the state of gelatination of the rubber. Investigations on this point have, however, not yet been carried so far that conclusions are possible in connection with the subjects treated in this book (composition, preparation

and properties of the rubber); nor have these methods, as yet, gained any importance in judging raw rubber or in determining its value for certain manufacturing processes. It may however be expected that this will form an important point of attack for further investigations.

On swelling phenomena see E. POSNJAK, *Kolloid-chemische Beihefte* III (1912), 417; F. KIRCHHOF, *Kolloid-chemische Beihefte* VI (1914), 1; D. SPENCE and G. D. KRATZ, *Z. Koll.* 15 (1914), 217; F. C. VAN HEURN, *Comm. Delft* III, page 105; H. P. STEVENS, *J. S. Ch.* I. 38 (1919), 193 T, also *I. R. J.* 58 (1919), 260 A. DUBOSC, *C. Gp.* 1917, page 9265, and *ibid.* 1919, pages 9781 and 9813.

A step further in the treatment of raw rubber, to obliterate outer irregularities for testing, is dissolving it. The exterior form is then wholly abolished, and the difficulties of mechanical tests, mentioned in § 230, are avoided; still the structure of the rubber may be supposed not to be broken down to such an extent as, for instance, during vulcanisation, so that the study of solutions may be expected to give valuable and independent indications.

The viscosity of rubber-solutions will be treated of in the next paragraphs. Another property of some importance is the velocity with which and the degree to which the rubber dissolves in different liquids, a point that has a direct bearing on certain manufacturing processes. In how far different methods of preparation affect these properties is, however, as yet incompletely known. That a preliminary treatment of the rubber (mastication etc.) may greatly influence the dissolving, is a well-known fact; that certain types of crepe-rubber dissolve more easily than other types of rubber, and that in some cases a fluid homogeneous solution is easily obtained, whilst in others jelly-like lumps remain undissolved, is often observed when making viscosity determinations as described in the next paragraphs.

Mechanical treatment generally facilitates the dissolving, as in other colloids also; but a method of expressing this property in figures has not yet been worked out, and the influence of different stages in preparation is as little known as the importance of differences in this respect for manufacturing purposes.

On the velocity with which rubber (in this case vulcanised rubber) takes up different liquids, see for instance G. FLUSIN, *Ann. de Chimie et de Physique* 13 (1908), 488; P. BARY, *C. R.* 161 (1915), 589.

V. HENRI (*Le Latex*, page 352 and 399) studied the solubility in benzene, the viscosity and the adhesiveness of rubber prepared by different coagulants. He found the method of coagulation, the duration of washing, the temperature and duration of drying, and the temperature at which the rubber is dissolved in benzene to be of influence on the results. Rubber obtained by evaporation dissolved with difficulty in benzene, and sometimes gave only a jelly-like mass and no liquid; coagulation by acids, or by mixtures of acetic acid and certain (unnamed) salts, gave rubber that dissolved very easily, especially when the rubber was not too much washed.

Similar observations were made by CL. BEADLE and H. P. STEVENS (*I. R. J.* 44 (1912), 554) who found that crepeing increases the speed of dissolving in benzene, but sheeting (passing through even speed rolls) gives a rubber which does not readily dissolve, but gives a jelly-like mass, as is also the case with the unwashed Hard Fine Para.

Whether fractional dissolving of the rubber may give a separation in different components, is not yet wholly settled; rubber is regarded by many authors as an emulsoid, which therefore consists of two phases of different properties.

On differences in viscosity of solutions obtained by fractional dissolving of rubber see § 233, page 574.

On a soluble and insoluble part in rubber see for instance W. A. CASPARI, *J. S. Ch. I.* 32 (1913), 1041; further D. F. TWISS, *Annual Report Soc. Chem. Ind. IV* (1919), 321.

Of course the separation of the „insoluble part“, the nitrogenous and other non-rubber constituents, is an other question (compare § 247).

The structure of rubber films obtained by evaporating its solutions may perhaps give further indications and deserves attention.

CH. FOX (*I. R. J.* 37 (1909), 23 and 97) distinguished different types of films obtained from a number of commercial brands by evaporating the naphta-solutions, but failed to find a definite film peculiar to any particular brand. The viscosity of the solutions appeared to play the principal role in determining the type of film.

PH.. SCHIDROWITZ (J. S. Ch. I. 28 (1909), 6, see also I. R. J. 37 (1909), 98) studied films obtained by evaporating benzene-solutions, and produced a pronounced net structure by short treatment with a benzene-solution of sulphur chloride.

H. P. STEVENS (J. S. Ch. I. 31 (1912), 1099, also I. R. J. 45 (1913), 168) compared rubber, which had been dissolved in benzene and freed from the insolubles, with the original sample. Though certain differences in rate of cure were observed (see § 247), the recovered rubber showed very normal properties after vulcanisation.

§ 232. Viscosity of rubber solutions.

As we said in § 231, rubber solutions may be expected to furnish data on properties of the raw rubber that are lost or changed after vulcanisation. The property of rubber solutions that has attracted most attention is certainly the viscosity, which has played a large role in judging rubber.

Viscosity determinations, in general, are used as a check on the state of polymerisation or molecular aggregation — in general on the colloidal status — of the dissolved substance. As the state of polymerisation is regarded by many authors as one of the most important factors that determine the properties of rubber, viscosity determinations were considered as a means of obtaining a direct insight into polymerisation and depolymerisation phenomena.

The state of affairs is, however, not so simple; it is not only the structural differences, the degree of aggregation or polymerisation of the rubber, that influences the viscosity of dilute solutions, but also (and to an important degree) the by-substances in the rubber, that so to say change the liquid in which the rubber is dissolved, and the surface-tension of rubber against solvent. These differences may be compared, to a certain extent, with the differences in viscosity obtained by dissolving one sample of rubber in different solvents.

As we shall see in § 235—237, this goes so far that in ordinary plantation-rubber (first quality crepe and sheet) viscosity determinations (at least in 1 % solution, as in our tests) are as much a check on the traces of by-substances in the rubber as on the constitution or degree of polymerisation of the rubber-hydrocarbon.

It can easily be shown that the viscosity of a 1% rubber solution is changed by adding traces of the various substances treated in former chapters. Shaking a benzene solution of rubber with one or two drops of the following chemicals may change its viscosity for instance from 30 to:

acetic acid	23
hydrochloric acid	15 $\frac{1}{2}$
formalin	27
ammonia	34
sodium acetate solution	33

that is in each case a similar change as when adding the chemicals to the latex before coagulation, or treating the wet or dry rubber with them.

When shaking a benzene-solution of rubber with a drop of dilute solutions of different chemicals, the effect is less marked, as only part of them is taken up by the benzol from the watery solution. Nevertheless the influence runs quite in the expected direction. For instance for a solution with a viscosity of 37:

water	37 $\frac{1}{2}$	dilute acetic acid	35 $\frac{1}{2}$
dilute ammonia	42	„ sulphuric acid	36 $\frac{1}{2}$
„ sodium hydroxyde	48 $\frac{1}{2}$	„ sodium bisulphite	35
„ sodium acetate	37	strong formalin	32

The point has not yet been followed up quantitatively (for instance by determining the amount of chemicals taken up by the benzene-solution) but the above figures may suffice to show that the presence of traces of chemicals is sufficient to explain changes in viscosity in many of the cases mentioned in this book.

On the effect of acids in lowering the viscosity of rubber solutions see D. SPENCE and G. D. KRATZ, Z. Koll. 14 (1914), 270; G. BERNSTEIN, Z. Koll. 15 (1914), 50; F. KIRCHHOF, Z. Koll. 15 (1914), 33.

A. VAN ROSSEM (Comm. Delft III, page 89) found no relation between the acidity of raw rubber and its viscosity.

K. GORTER (Med. Rubber IV, page 35) showed that the viscosity is decreased by adding iso-amylalcohol or creosote to the solution; acids such as acetic acid and iso-butyric acid gave a marked decrease. Benzol from which traces of thiophen had been removed by shaking with sulphuric acid gave too low values for viscosity, but after remaining on pieces of sodium hydroxyde for one night this benzol again gave normal values.

For viscosity determinations different solvents may be used; they give different figures, and the results for different samples of rubber do not run strictly parallel. Whether

determining viscosity in several solvents side by side might bring to light a new property of rubber, not to be learnt from a 1 % solution in benzene only, remains to be investigated.

F. KIRCHHOF (Z. Koll. 15 (1914), 30) found the time of flow of a 1% solution to differ from 29 to 166 seconds for different liquids.

See further for instance H. J. HELLENDORF (Comm. Delft III, page 92), R. GAUNT (J. S. Ch. I. 33 (1914), 448 and 451, also I. R. J. 47 (1914), 1045 and 1093) and others, especially the review in A. DUBOSC and A. LUTTRINGER, *Le Caoutchouc, sa Chimie nouvelle, ses Synthèses*, page 229.

§ 233. Determination of Relative Viscosity.

Viscosity, in this book, is expressed as relative viscosity and determined after a method which, after careful study, has been fixed and adopted by the Rubber Experimental Stations in the Dutch Indies. In brief words viscosity is expressed as the relative viscosity at 30° C of a 1 % solution (in weight) of rubber in benzene.

The full prescription is given in Arch. 4 (1920), 122; also I. R. J. 59 (1920), 1197.

The following points are of some importance from a general point of view.

The rubber is examined in the air-dry state; a recalculation for moisture-content is not made. Drying the rubber previously has to be avoided, as this may cause the viscosity to increase greatly.

The following figures for two samples of which finely cut portions (as they are used for viscosity determinations) were placed in a desiccator above quicklime, illustrate this phenomenon clearly:

	I	II
Viscosity of original air-dry sample	35	34
" after 3 days keeping above quicklime	48 ¹ / ₂	49
" 7 " " " "	72 ¹ / ₂	80
" 19 " " " "	80	—

The samples remained in the desiccator for two months and were then placed in the air, so that they took up moisture again. The viscosity kept its very high values for sample I (55, 67, 108 after 1, 4 and 11 weeks), but decreased to lower values (43, 46, 47) for sample II.

Five samples of smoked sheet gave the following figures:

	A	B	C	D	E
Air-dry	31 $\frac{1}{2}$	32	27	39	37
Dried 3 days above quicklime. .	43	51	35	36	42 $\frac{1}{2}$
Dried 3 days above sulphuric acid	68	80	58	27	35

The increase from drying above sulphuric acid may therefore be much greater than above quicklime, though in other cases no increase or even a decrease was found. The causes of this different behaviour have not yet been cleared up; it may be that certain volatile substances are removed from the rubber, but it may also be that a pectisation on drying plays a role. The dry samples generally do not dissolve easily in benzene, and leave jelly-like clumps, which, of course, remain on the filter before the viscosity determination.

It may be added that in many other cases the differences were not so large as above, but an increase from 35 to 45 on drying is quite common.

Further investigations would be necessary to clear up these interesting phenomena, but the above figures are sufficient to show that drying the sample before determining the viscosity should be avoided, as it brings with it unknown complications.

The solution of rubber in benzene has to be protected against strong daylight or sunlight, as the viscosity decreases appreciably even during determinations in too strong daylight, the successive readings giving decreasing values for time of flow, so that no reliable average figure is obtained.

For examples of the decrease in viscosity on keeping the solutions see H. W. Woudstra (Z. Koll. 5 (1909), 32) and J. G. Fol (I. R. J. 45 (1913), 680, also C. Gp. 1913, page 7064, and Z. Koll. 12 (1913), 144).

F. C. van Heurn (Comm. Delft III, page 86) proved that light is the factor which causes the decrease in viscosity when taking successive readings with one solution. See also R. Gaunt, J. S. Ch. I. 33 (1914), 450; also I. R. J. 47 (1914), 1094.

Kept in a closed chest or box at room temperature (27° C) the solutions, however, may retain the same viscosity for 1 or 1½ month at least, as we repeatedly found in control-tests.

The use of bottles of brown glass instead of white did not give us any advantage; the viscosity was exactly the same. We did not, however, investigate as to whether a solution kept in a brown bottle can stand daylight better.

The temperature during the keeping of the solution seems to be without influence on the results. Parts of the same solution were kept for three days in the laboratory room (26—31°), in the boiler room (temperature of the solution up to 34°) and in a cool place (temperature not above 25°.5), but the viscosity was found exactly the same.

Heating the solution to higher temperatures gives a decrease in viscosity, see § 236, page 594

Whether the dissolving process is aided by shaking the bottles by hand from time to time or often, or by placing them for two days on a shuttle machine, has no influence on the results, provided the solution is kept in the dark.

J. G. FOL (I. R. J. 45 (1913), 741, also C. Gp. 1913, page 7068, and Z. Koll 12 (1913), 145) in one series of experiments found an increase in viscosity on shaking the solution, but this result must have been due to some special circumstance, as F. C. VAN HEURN (Rubb. Rec. 1914, 450; Comm. Delft III, page 85) found shaking the solution in the dark for 7 and 14 hours without influence on the viscosity, while K. GORTER (Med. Rubber IV, page 33) also found shaking by hand or on the machine to give the same results.

Numerous further control-experiments have confirmed the above conclusion that shaking from time to time by hand, or continuously on the machine has no influence on the figures for viscosity.

The rubber does not completely dissolve in benzene. Many samples of crepe dissolve easily and quickly, only leaving a thin powdery deposit; others dissolve slowly and leave small lumps, which are invisible in the solution, but become visible when they adhere to the walls of the bottle after the solution has been moved. Still other samples of crepe dissolve with difficulty and leave much of a jelly-like

mass, the concentration of the solution being only 0.7 or even 0.6 instead of 1 %. In the latter case the result of the viscosity determination becomes dubious, and low values are generally found.

With smoked sheet the dissolving process is mostly slower; the small pieces in which the sample is cut remain visible, and the brown films of the superficial smoky layers remain a long time undisturbed, especially if the solution is only shaken from time to time by hand. Whether these dissolving phenomena might in some way or other be used to get an insight into the state aggregation of the rubber, is not yet known (see § 231).

Within moderate limits these differences in dissolving and the amount of jelly-like lumps that remain on the filter have no influence on the results; only in cases when a large part of the sample has not gone into solution are deviating (too low) values for viscosity found.

J. G. FOL (I.R.J. 45 (1913), 681, also C. Gp. 1913, page 7067, and Z. Koll. 12 (1913), 145), found a lower viscosity when the rubber was imperfectly dissolved, and advises the dissolving of the rubber as completely as possible.

F. C. VAN HEURN (Comm. Delft III, page 89) in an experiment with Hevea-crepe found the part that dissolved most rapidly to have a lower viscosity than the rest, when the first fraction only contains a small part of the rubber. When the bulk of the rubber (some 90 %) was dissolved, further shaking gave no increase in viscosity.

H. P. STEVENS (I.R.J. 46 (1913), 345) found the viscosity of four fractions, obtained by treating sheet rubber with four successive quantities of benzene, and testing after twelve months standing in a dark cupboard, to differ markedly, the later fractions showing a much higher viscosity. This could however, at least partly, be explained by the lower resin-content.

The dimensions of the viscosimeter have an influence on the results. The prescription referred to above adopts an Ostwald viscosimeter with a capillary of 0.8 — 0.9 mm diameter and a time of flow for pure benzene at 30° C of 10—13 seconds. For routine testing we often use a viscosimeter with a wider capillary and a more rapid flow (5—8 seconds), as this allows of more determinations being done in one day.

The theoretical relationship between the times of flow in different instruments is not yet completely known; for practical purposes a sufficiently accurate correction is obtained by multiplying the relative viscosity with a factor (in the above case 1.075) obtained by comparing accurately the times of flow of several rubber-solutions in both the standard and the other instrument. The wider capillary gives a lower value for relative viscosity.

For tests in viscosimeters of different dimensions see J. G. FOL, I. R. J. 45 (1913), 679, also Z. Koll. 12 (1913), 142, and C. Gp. 1913, page 7063.

K. GORTER in his determinations of viscosity index used a viscosimeter of the pipette type (see Med. Rubber IV, page 9; Teysm. 26 (1915), 304). Such a viscosimeter cannot be kept at constant temperature; but the room temperature in Buitenzorg is sufficiently constant to allow of its use. The cleaning of this instrument is more easy, and further operations are also somewhat simplified by its use.

A pipette viscosimeter was also proposed by V. HENRI (Le Latex, page 408), while G. BAUME and H. VIGNERON (C. Gp. 1920, page 10331) used a pipette viscosimeter in a constant temperature bath. See on their use for celluloid H. SCHWARZ, Z. Koll. 12 (1913), 32, and others.

The viscosimeter is placed in a water bath of 30° 0 C; higher temperatures, of course, give a quicker flow of the solution, lower temperatures increase the time of flow. For the range of temperatures between 30° and our room temperature (27°) we found the following differences in time of flow.

Sample	A	B
Time of flow at 30° 0	321.7 sec. = 100	254.2 sec. = 100
" " " " 29° 0	101.8	101.0
" " " " 28° 0	103.6	102.8
" " " " 27° 0	105.0	104.2
Again brought to 28° 0	103.6	102.7

A difference of 0° 1 in temperature of the bath therefore causes a difference of 0.1—0.2% in viscosity, or about

0.05 unit for ordinary samples, so that the temperature of the bath, which can be easily kept constant, will not be the cause of serious errors.

PH. SCHIDROWITZ (Rubber, page 161) mentions that a difference of 1° gives an error of approximately 1 unit in the relative viscosity, with which our above figures agree sufficiently.

J. G. FOL (I. R. J. 45 (1913), 680, also C. Gp. 1913, page 7064 and Z. Koll. 12 (1913), 143) found the relative viscosity, taking into account the difference in time of flow of pure benzene, to be approximately constant between 20° and 75° C.

§ 234. Other methods of determining and expressing viscosity.

Viscosity determinations attracted a lot of attention in former years, as a direct insight was expected from them into the degree of polymerisation of the rubber. When it was found that viscosity determinations bear no direct relationship to the properties after vulcanisation, most investigators dropped their use. We do not intend to review all that has been done in this field, but will restrict ourselves to the description of two methods which have played a role in the investigations dealt with in this book, viz. the determination of the viscosity number and of the viscosity index.

For a review of older investigations on this point see, for instance, J. G. FOL, I. R. J. 45 (1913), 578, 627, 679 and 741; also C. Gp. 1913, page 6970, also Z. Koll. 12 (1913), 131. See further CL. BEADLE and H. P. STEVENS, I. R. J. 45 (1913), 1081; PH. SCHIDROWITZ and H. A. GOLDSBROUGH, I. R. J. 45 (1913), 886, also Z. Koll. 13 (1913), 46.

Viscosity Number.

The viscosity number, as it was used by the Government Institute at Delft, is the surface contained between the curve of relative viscosities for solutions from 0 to 1 gm rubber per 100 cc benzene, the abscissae, and the ordinates for concentrations of 0 and 1 gm. This manner of expressing viscosity therefore takes into account the form of the curve for relative viscosity, and as such is a more complete

method of expression than the relative viscosity or the viscosity index, which give figures for one ordinate only. It has been, however, proved that the curves for relative viscosity for different samples of rubber never intersect, so that they change in form after a well defined, be it as yet unknown law. From this it follows that the form of the curve is wholly determined by the ordinate for a fixed concentration; and as the determination of a surface, especially with one curved side, is somewhat complicated and not so exact as the determination of one ordinate, the expression as relative viscosity was preferred as more simple and easy.

Originally, in the determination of the viscosity number, three solutions of different concentration were used, of which two were mostly prepared by diluting the most concentrated one, which was made up to a concentration of about 1 gm rubber per 100 cc benzene. Through the three points for relative viscosity thus obtained a curve was drawn freely by hand, and a piece of thin cardboard, representing the surface between curve, axe of abscissae and ordinates of 0 and 1 %, was cut out and weighed, or the surface was determined by a planimeter.

See J. G. FOL, *I.c.* and *Teysm.* 24 (1913), 119.

Though one operator obtained in course of time a considerable experience in drawing the curve, some uncertainty, of course, remained in the results, especially between determinations in different institutes.

As the experimental material increased, it was found that curves for different types of rubber (if determined with sufficient accuracy) never intersect, and that a set of standard curves could be drawn for increasing relative viscosities at a fixed concentration, which showed a gradual and regular change in form.

A. VAN ROSSEM, *Comm. Delft III*, page 83.

Once this set of curves was fixed, a determination of relative viscosity at one arbitrary concentration was sufficient, to find which curve belonged to the sample in question and what was therefore its viscosity number. This simplified the determination greatly, but at the same time took away

the argument for using the whole curve (the surface) instead of the ordinate of one point of it, the relative viscosity.

The theoretical relation between viscosity number and relative viscosity at 1%, from which the exact, mathematical form of the curves for relative viscosity might be derived, has not yet been worked out.

A. VAN ROSSEM (Comm. Delft III, page 82) gives the following relation between relative viscosity at a concentration of 1% (1 gm per 100 cc benzene) and viscosity number:

Relative Viscosity	Viscosity Number
19.5	40
29.5	50
39.5	60
49.5	70
59.5	80
69.5	90
79.5	100

When using for both viscosity number and relative viscosity a concentration of 1% in weight, we found the following relation:

R. V.	V. N.	R. V.	V. N.
5	15½	50	72½
10	22½	55	78
15	29	60	83
20	36	65	88½
25	42½	70	94
30	49	75	99
35	55	80	104
40	61	85	109
45	66½	90	114

Viscosity Index.

The viscosity index, is the logarithm of relative viscosity at a concentration of 1 gm rubber in 100 cc benzene. It was found that the values for logarithm of relative viscosity over a range of concentrations in the neighbourhood of 1% lie very nearly on a straight line, which moreover, for different samples of rubber, passes through one fixed point (A in Fig. 25). The form of the whole curve is parabolic, as it starts from the origin of axes (the relative viscosity

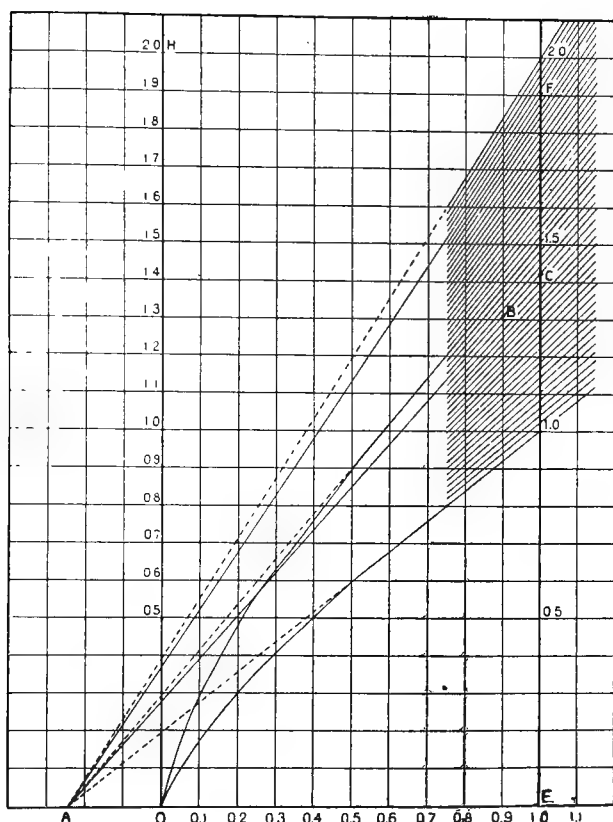


Fig. 25.
Curves for logarithm of relative viscosity and lines used
in the determination of viscosity index.

of a 0% solution — pure benzene—being 1 and its logarithm therefore 0); but at concentrations of above 0.6% it becomes very approximately a straight line.

Fig. 25 depicts the manner of deriving the viscosity index. When the logarithm of relative viscosity at an arbitrary concentration near 1%, say at 0.9, is found to be 1.30, then the thus found point B is simply connected with A by a straight line, and the point C, where AB cuts EF, the ordinate for 1%, gives the viscosity index 1.42. In actual practice a set of lines as in Fig. 25 are drawn beforehand, so that by plotting logarithm of relative viscosity against concentration the viscosity index is directly read.

The viscosity index was introduced by K. GORTER, *Teysm.* 26 (1915), 298, and *Med. Rubber IV* (1915). GORTER from some determinations at first assumed a fixed point not on the abscissa, but on the ordinate OH at 0.3 from the origin. Further investigations showed this assumption to be false, the lines AC, AF etc. cutting OH at different heights. From further determinations the point A at a concentration of -0.25 was then taken as the fixed point, and GORTER expressed the curve for logarithm of relative viscosity as $y = V.I. \times 0.8$ (x = concentration, y = logarithm of relative viscosity at that concentration, V.I. = viscosity index or logarithm of relative viscosity at 1% concentration) from which $y \frac{dx}{dy} = 1.25 x$, that is EA is a constant.

In a series of experiments we found the logarithms of relative viscosity to form straight lines as approximately as might be expected within the errors of determination; these lines were found to cut the abscissa at -0.11 to -0.22, on the average -0.174 (gm per 100 cc) and not at -0.25. One sample of very inferior earth-rubber gave an intersection at -0.03, so that the fixed point A, used in deriving the viscosity index, seems to be an approximation rather than a fact.

R. GAUNT (*J. S. Ch. I.* 30 (1914), 450; also *I. R. J.* 47 (1914), 1093) also observed that the logarithms of relative viscosity lie on a straight line, and proposed to use the inclination of these lines with the abscissa as a means of expressing viscosity.

The advantages of this method of expression over the viscosity number in its old form are evident: one determination at a concentration near 1 % is sufficient (instead of three at different concentrations), no curve need be drawn, and Fig. 25 gives a direct reading of the viscosity index. As the lines AB etc. are straight, even concentrations differing considerably from 1 % give sufficiently accurate results; concentrations of about 0.8 % give a much more rapid flow in the viscosimeter and therefore allow of more determinations to be made in a certain time. These advantages, however, lost their significance when a set of standard curves for relative viscosity had been drawn up, and the relative viscosity at a concentration of 1 % in weight was then chosen as the simplest form of expression.

We have expressed viscosity as viscosity index in our work up till January 1, 1920; some of the data in this book are

still given in this form (compare Fig. 3 page 105, and the table on page 130; further Figs. 26 and 27).

The relation between viscosity index (logarithm of relative viscosity at a concentration of 1 gm in 100 cc benzene) and relative viscosity (at a concentration of 1 % in weight) — using the fixed point A at -0.25 — is:

V. I.	R. V.	V. I.	R. V.
0.50	2.8	1.50	22.05
0.75	4.7	1.60	27.1
1.00	7.85	1.70	33.35
1.10	9.65	1.80	41.0
1.20	11.85	1.90	50.35
1.30	14.55	2.00	61.95
1.40	17.9		

This relation is, however, not the one to be used in comparing our former and present results, because the viscosity index was determined in viscosimeters⁹ with a somewhat more rapid flow (wider capillary) than the standard adopted for relative viscosity (compare § 233). The following table may be used to recalculate the data in our older publications, though the results are only approximate and may differ 1 or 2 units from the real value of relative viscosity, when the concentration differed much from 1 %, because in the correction of relative viscosity at concentrations differing from 1 % curves are used that do not correspond with the fixed point A at -0.25 gm per 100 cc, but with a fixed point nearer to the origin (-0.20 % in weight). This source of error, however, in most of our determinations is of little importance, because in the determination of the viscosity index we actually used concentrations of 0.85 to 0.90 gm per 100 cc, or nearly 1 % in weight, because these give a more rapid flow.

Table for the recalculation of viscosity index, as used in the Central Rubberstation, to relative viscosity at 1 % in weight:

V. I.	R. V.	V. I.	R. V.	V. I.	R. V.
0.50	2.95	1.40	18.9	1.80	43.3
0.75	4.95	1.45	21.0	1.85	48.0
1.00	8.25	1.50	23.2	1.90	53.1
1.10	10.2	1.55	25.8	1.95	58.9
1.20	12.5	1.60	28.6	2.00	65.3
1.25	13.9	1.65	31.7	2.05	72.5
1.30	15.4	1.70	35.2	2.10	80.2
1.35	17.0	1.75	39.0	2.20	98.7

See more extensive tables in Arch. 4 (1920), 130 and 131; also I.R.J. 59 (1920), 1199.

§ 235. Relation between viscosity and other properties.

As we determine viscosity regularly in every sample that is tested, a large material is at hand to study the relationship between viscosity and other properties. A discussion of this point is the more important as viscosity has been assumed by some authors to be a gauge either of tensile strength or of rate of cure, so that in their eyes the complicated vulcanisation-testing might be replaced by a more simple viscosity test. We shall see in this paragraph that viscosity is affected by so many factors that the direct relationship to any other property is in general wholly obscured; in § 237 we will discuss the use of viscosity determinations in the testing of raw rubber.

From the data mentioned in this book the following summary may be compiled as to the relation between viscosity and properties after vulcanisation.

Viscosity and tensile strength.

We have enumerated in § 201 a number of cases in which the tensile strength decreases; these cases affect the viscosity in the following manner.

1) Rubber from very young trees, which shows a low tensile strength (and a great rate of cure), ordinarily shows a low viscosity (§ 24).

2) Whether tapping pollarded trees causes a decrease in tensile strength, is not yet quite certain (§ 36); a drop in viscosity was always found in such cases.

These are the data available on the influence of the state of the tree; so far as they go, a decrease in tensile strength (which, in such cases, may be supposed to be due to a change in the principal components of the colloidal rubber complex) seems always to be accompanied by a decrease in viscosity.

The same conclusion may be drawn from cases in which the tensile strength diminishes by deterioration of the rubber by external factors. For instance:

3) The decrease in tensile strength by heat (be it rather high temperatures, such as above 85° C, or a long exposure to somewhat lower temperatures such as 70° C) is always accompanied by a marked decrease in viscosity (§ 125, 145 and 165).

4) Deterioration in tensile strength by micro-organisms (see § 168 and 183) is always accompanied by a marked decrease in viscosity.

5) Deterioration by sunlight (§ 164) or tackiness caused by copper salts (§ 169) also have a large effect on viscosity.

6) The decrease in tensile strength caused by excessive quantities of some coagulants, which in a case such as sulphuric acid can probably not be ascribed to the longer time of cure alone (§ 86), is accompanied by a marked decrease in viscosity; in the case of alum (§ 88), where the tensile strength after the use of large doses does not decrease more than one would expect on account of the much prolonged cure, the decrease in viscosity is much smaller.

Compare also O. DE VRIES, Arch. 4 (1920), 173, 176 and 177.

While these cases all lead to the conclusion that a deterioration which results in a decrease in tensile strength is always accompanied by a decrease in viscosity, there is at least one case that contradicts this conclusion and warns one against general conclusions of too sweeping a nature. We refer to partial coagulation, which gives a first clot with a lower tensile strength, a greater rate of cure and a higher viscosity than the rest. It may, of course, be that the decrease in viscosity, accompanying the decrease in tensile strength, is in this case more than overtaken by the increase in

viscosity caused by the substance which also gives an increase in rate of cure; but no facts are as yet available which furnish proof of this point.

By carefully washing and recrepeing the rubber we made sure that particles of dirt, eventually included in the first clot, are not the cause of the lower tensile strength in this case, see Arch. 1 (1917), 181 and 186.

Cases of an increase in tensile strength, other than the reverse of the above mentioned examples, are not known, and no conclusions are therefore possible as to whether such an increase is or is not accompanied by an increase in viscosity.

That changes in viscosity are very often not accompanied by a change in tensile strength, will be evident from the following pages, in which the factors affecting both rate of cure and viscosity are reviewed. It will there be seen that many chemicals, and further many chemical changes in latex or coagulum, affect rate of cure and viscosity but leave the tensile strength unchanged.

There are further some cases in which the viscosity changes, while both tensile strength and rate of cure remain the same. We may mention:

1) Some chemicals, for instance alcohol as a coagulant (§ 99) leave tensile strength and rate of cure unchanged, while the viscosity decreases; in the case of alcohol a decrease in slope is also observed.

2) Heating to not too high temperatures, by which the rubber becomes somewhat weak and sticky on the surface, gives a decrease in viscosity long before tensile strength or rate of cure show any change (§ 125, 145). The low viscosity of smoked balls (§ 189) or of rubber prepared after the Kerbosch-process (§ 193) is probably another example of this case.

3) Apart from rubber of very young trees, which has a low tensile strength and viscosity, one sometimes meets with sheet-rubber which in the raw state is more or less brittle (snaps more or less easily when stretched by hand, which defect is mostly called „shortness”). Such rubber shows a somewhat low viscosity, but a normal tensile strength after vulcanisation (compare § 105 and 230). This type of rubber is often traceable to relatively young trees, as mentioned in § 24; whether this always offers the

explanation is not yet certain. A deficiency in the raw state, perhaps caused by some difference in the state of gelatination, is apparently restored during vulcanisation.

Reviewing these data we may conclude that a certain relationship between viscosity and tensile strength seems to exist, in so far as a decrease in tensile strength is mostly, if not always, accompanied by a decrease in viscosity. The many factors, however, which affect viscosity and leave tensile strength unchanged make it that in ordinary plantation-rubber the correlation between viscosity and tensile strength is relatively small, and that conclusions from viscosity determinations as to tensile strength are not feasible.

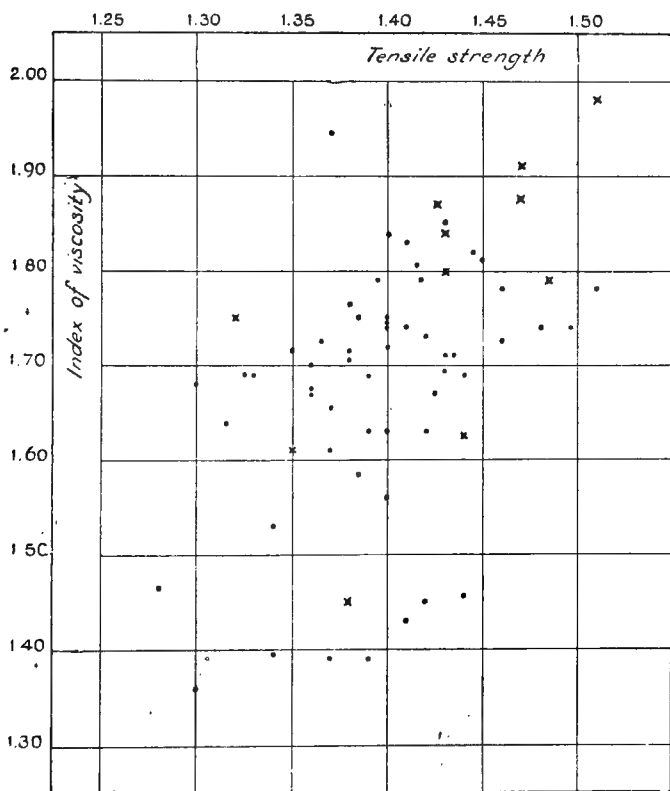


Fig. 26.

Viscosity (expressed as viscosity index) and tensile strength of a number of samples of first quality crepe (dots) and smoked sheet (crosses).

Fig. 26 depicts the relation between tensile strength and viscosity for a number of samples of smoked sheet and first quality crepe from estates; we did not calculate the coefficient of correlation, but it will be clear that the correlation, if existing, is very small. A tensile strength of 1.40 KG per mM^2 may be combined with a viscosity of 1.39 to 1.83 (relative viscosity $18\frac{1}{2}$ to 46), that is about the lowest and highest values for ordinary rubber.

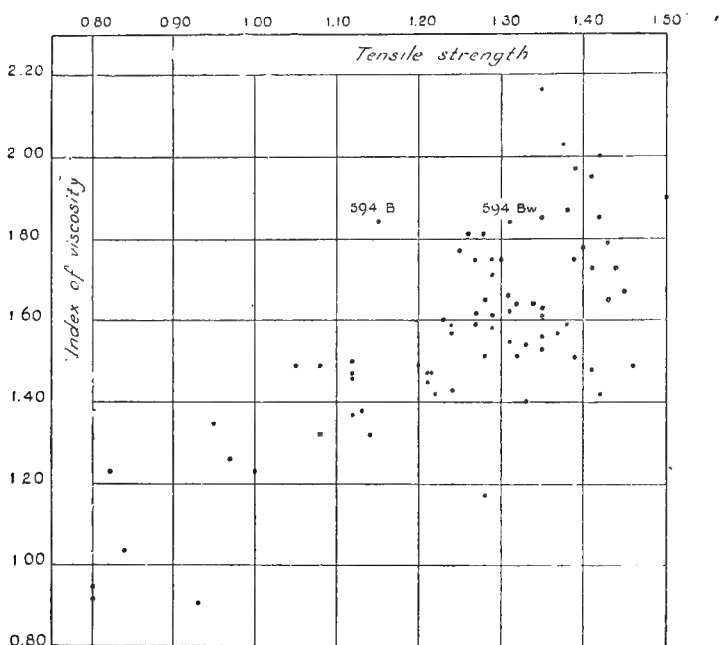


Fig. 27.

Viscosity (expressed as viscosity index) and tensile strength of a number of samples of lower grade.

Somewhat more of a correlation comes to light when plotting viscosity and tensile strength for a number of samples of lower grade, as in Fig. 27. An increase in viscosity with increasing tensile strength is, in a general sense, to be observed, though the deviations are too large to allow of any conclusions. A viscosity of 1.50 (relative viscosity 23) may be found in a rubber with a tensile strength of 1.05 KG per mM^2 (i.e., very low) but also

of 1.46 KG per mm^2 (i.e., excellent for lower grades). As, however, in the very poor types a real deterioration of the rubber has mostly taken place from some of the causes discussed on page 583 a nearer relation between viscosity and tensile strength in the lower than in the first grades is not unexpected.

K. GORTER (Med. Rubb. IV, page 46) reduced the tensile strength, found after a fixed cure of $1\frac{1}{2}$ hours in the Government Institute at Delft, to a state of cure with a coefficient of vulcanisation of 3.5. He concluded that a relationship exists between this reduced tensile strength and the viscosity of the raw rubber (tensile strength being equal to the viscosity index multiplied by 70). When plotting this reduced tensile strength against viscosity index it is, however, easily seen that the correlation, if existing, is very small.

Viscosity and rate of cure.

The numerous factors which affect the rate of cure of plantation-rubber to a small or larger degree always cause a change in viscosity also; but the changes do not run parallel in all cases. From the material at hand the following summary may be composed.

1) Rate of cure and viscosity both increase:

by the use of chemicals such as sodium sulphite (§ 44), sodium bisulphite (§ 48), sodium carbonate (§ 45), sodium acetate (§ 52);

by the changes which slowly take place in moist coagulum, for instance when the coagulum is rolled on the day following coagulation as compared with rolling some hours after coagulation (§ 117 and 135); when drying slowly (§ 124 and 144); when making the sheets or crepes rather thick, so that they take longer to get dry (§ 121 and 137); when keeping the moist coagulum, so that maturation takes place (§ 108); when applying spontaneous coagulation or coagulation with sugar (§ 94—96);

by fractional coagulation (§ 176), the first clot giving a quicker curing rubber with a high viscosity.

2) Rate of cure and viscosity both decrease:
by diluting the latex (§ 64);

by the use of chemicals such as formalin (§ 43), sodium thiosulphate (§ 49), acetic acid (§ 83), sulphuric acid (§ 86), formic and other acids (§ 87 and 89), alum (§ 88);

by all factors which prevent or retard the changes in moist coagulum, such as rolling the coagulum soon after coagulation, rolling thin, drying quickly, using disinfectants such as formalin, bisulphite, acetic acid etc. in the preparation of matured rubber;

by soaking the freshly rolled sheets or the coagulum in water, in which case a short soaking gives a relatively large decrease in rate of cure and a small decrease in viscosity (§ 139);

by treating the coagulum with hot water, in which case the decrease in viscosity may be large, the decrease in rate of cure relatively small (§ 140).

All cases enumerated under 1 and 2 may be readily explained by the influence of traces of chemicals or of by-substances which act as accelerators during vulcanisation and affect viscosity in the manner discussed in § 232. In the above cases the effect on rate of cure and viscosity runs parallel, that is rate of cure and viscosity both increase or decrease; it can be easily proved that it is indeed traces of chemicals which work in such cases, by adding small amounts of them to the rubber-sulphur mixture before vulcanisation (see § 43, page 87; § 88; § 89, page 187 etc.) and to the solution to be tested on viscosity (see § 232). The well-known rule that acid substances retard vulcanisation and decrease viscosity, while alkalis are accelerators and increase viscosity, offers an explanation in most if not in all cases. Whether substances exist that accelerate vulcanisation but give a decrease in viscosity in dilute solution and vice versa is not yet known; the possibility of a decomposition at the high temperature of vulcanisation, so that a modified catalyser is then at work, has also to be considered.

3) Rate of cure increases and viscosity decreases, and vice versa, in the following cases.

Coagulation of latex by heat gives a rapidly curing rubber with a low viscosity (§ 100). Some other methods of coagulation, in which heat plays a role, have a similar effect; for instance preparing smoked balls after the Brazilian method (§ 189) or preparing dried up latex after the Kerbosch-process (§ 193).

Older trees give a slower curing rubber with a higher viscosity (§ 24).

After opening a tapping cut on trees that have had a period of rest the rubber gradually shows an increase in rate of cure, while the viscosity decreases (§ 29).

Heavy tapping causes an increase in rate of cure and a decrease in viscosity (§ 30—32); tapping pollarded trees has the same effect (§ 36).

Individual trees often show a high viscosity combined with a quick curing rubber and vice versa (§ 22).

The first case of this series may represent a complicated phenomenon: the increase in viscosity caused by the substances that cause the greater rate of cure (if, indeed, such substances are present) may be nullified and overtaken by the decrease in viscosity caused by the heat.

The other cases all range under changes in the physiological condition of the trees, and it seems to be quite a general rule that physiological factors cause an increase in rate of cure combined with a decrease in viscosity, or vice versa. Whether this is due to some by-substance in the rubber, or to a change or lower degree of polymerisation of the rubber itself, is not yet known. For practical testing purposes this contrast between factors ranging under „preparation” and under „condition of the trees” is of some importance, as we will see in § 237.

From the above enumeration it will be clear that a simple relation between viscosity and rate of cure does not exist. In most cases the preparation causes parallel changes in both properties; but then, the more methods of preparation become standardised on estates, the more deviations ranging under this head will retire to the background, and the more

the condition of the trees will have to be looked into as the source of variability and deviations.

The examples given on pages 330 and 331 clearly show that in estate samples rate of cure and viscosity do not run parallel; this may also be further shown by plotting the viscosity of a large number of samples against rate of cure, in which case no correlation comes to light.

See O. DE VRIES, Arch. 2 (1918), 470 and 485. Examples that there is no relation between the changes in rate of cure and in viscosity for estates preparing crepe-rubber see O. DE VRIES Arch. 2 (1918), 471; O. DE VRIES and W. SPOON, Arch. 3 (1919), 257, 259, 261 and 262.

A. VAN ROSSEM (Comm. Delft III, page 101) calculated the coefficient of correlation between viscosity and coefficient of vulcanisation after a $1\frac{1}{2}$ hours cure, and found values of 0.536 to 0.630 for first latex crepe and sheet, and 0.517 when including lower grades. This indicates a distinct, though rather low correlation between viscosity and rate of cure in such cases.

Viscosity and slope.

Taking up again the factors which affect slope, which have been enumerated in § 202, the following may be said about the accompanying changes in viscosity.

1) Continued tapping on trees that have had a rest causes an increase in slope, a decrease in viscosity (and an increase in rate of cure). See § 29.

2) Heavy tapping has the same effect (§ 32).

3) Sulphurous acid, which gives a decrease in slope, causes a small increase in viscosity and leaves the rate of cure unchanged (§ 52). Sodium sulphite and bisulphite, which also give a decrease in slope, give a greater increase in viscosity combined with an increase in rate of cure (§ 44 and 48).

4) Coagulation with alcohol gives an increase in slope and a decrease in viscosity (§ 99), whilst it leaves tensile strength and rate of cure unchanged.

5) Maturation of the coagulum gives a decrease in slope and a marked increase in viscosity, combined with a marked increase in rate of cure (§ 108).

6) Strong heating of the fresh, still wet coagulum may

cause the slope to increase; the viscosity decreases markedly already before a change in the other properties sets in; the rate of cure may also decrease by strong heating (§ 120 and 140).

7) Lower organisms causing spots on crepe may produce an increase in slope, a marked decrease in viscosity and a decrease in tensile strength and rate of cure (§ 168).

8) Copper salts cause the slope to increase, the tensile strength, viscosity and rate of cure to decrease (§ 169).

Definite conclusions as to a relationship between viscosity and slope are not yet possible, because in so many cases either rate of cure or tensile strength are also affected and may explain wholly or partly the change in viscosity. None of the above examples, however, contradicts the conclusion that an increase in slope (decrease in resistance to stretching) is accompanied by a decrease in viscosity and vice versa, and it may be that further research will indeed prove such a relationship to exist.

Viscosity and mechanical properties of raw rubber.

A relation between the viscosity and the mechanical properties (strength etc.) of the raw rubber might perhaps be expected sooner than with the properties after vulcanisation, during which so much is changed in the rubber. A parallelism between viscosity and strength of raw rubber has several times been observed, but extensive data are still lacking, probably owing to the difficulty of tests on raw rubber (see § 230).

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (J. S. Ch. I, 28 (1909), 3; also I. R. J. 37 (1909), 215) in a few samples found the viscosity in dilute solution and the mechanical properties or nerve of the raw rubber (breaking strain and resiliency) to run approximately parallel.

F. C. VAN HEURN (Comm. Delft III, page 98) found a direct ratio between viscosity and breaking load of raw rubber, when heating the rubber either at 130° C in an atmosphere of carbon dioxide, or at 100° in the air, or plasticising it on the mixing rolls: the decrease in viscosity and breaking load in all cases was nearly proportional. The same was the case after heating 10 hours at 100° C in carbon dioxide, which treatment increased both viscosity and tensile strength.

§ 236. Factors that influence viscosity.

From the review given in the foregoing paragraph three groups of factors that influence viscosity stand out clearly, namely:

1) a not very deep going desaggregation or depolymerisation which affects viscosity, but leaves the properties after vulcanisation unchanged.

2) chemicals or catalysers, which affect rate of cure and viscosity.

3) factors that cause deep going changes in the rubber itself, be it a decomposition or oxydation, or some other reconstruction of the principal colloids, which cause a decrease in viscosity besides a deterioration in tensile strength and a decrease in slope, but need not affect the rate of cure.

Under the *first* head may be brought changes by which the physical state of the rubber is altered, without either its chemical composition or the chemical structure of the complex of colloids being changed. Though the comparison is halting like every one of its kind, one might as an example think of the gravel-bed on a road, which shows a certain resistance and coherence as long as gravel, sand, clay and moisture form one compact mass of particles firmly adhering to each other, but changes to a loose heap when disturbed — without anything being altered in the gravel, sand or clay itself.

Changes as here meant are effected by the mastication of the rubber-sulphur mixture on the rolls which causes a marked decrease in viscosity, but (unless excessive) leaves tensile strength and rate of cure unchanged (see § 211, page 504).

F. AHRENS (Chem. Ztg. 34 (1910), 266) found that a 10 % solution of untreated Para-rubber had the same consistency and adhesiveness as a 18 % solution of rubber that had been masticated on hot rolls for some time. The latter solution was oxydised much more rapidly either during keeping or under the influence of ultraviolet rays.

J. BOUTARIC (C. Gp. 1911, page 4965) made viscosity determinations of 2 % solutions of a Para-rubber which had been kneaded on hot rolls and found the viscosity to decrease by continued mastication.

Similar observations were made by J. G. FOL and F. C. VAN HEURN (Comm. Delft IV, page 112), F. C. VAN HEURN (Comm. Delft III, page 97) and R. GAUNT (J.S. Ch. I. 33 (1914), 447, also I. R. J. 47 (1914), 1046).

G. BERNSTEIN (Z. Koll. 12 (1913), 194) studied the effect on viscosity of heating the rubber on the mixing rolls to 80° C for different lengths of time, and found the viscosity to decrease markedly in all cases, and to reach the same final low value after different times of rolling.

CL. BEADLE and H. P. STEVENS (I. R. J. 48 (1914), 530) found the viscosity to be enormously influenced by the mechanical treatment to which the rubber has been subjected beforehand.

These authors (Rub. Ind. 1911, page 270) hold the film or network of proteins to be impervious to benzene and to hinder the solution of the rubber, so that it must be broken up (by mastication etc.) beforehand.

In many of the above mentioned cases it has, however, not been investigated as to whether the treatment on hot rolls etc. left the properties after vulcanisation unchanged, so that deeper going changes, such as described in § 211, may in some cases have taken place.

Mechanical treatment of the rubber, such as in the ordinary tests, seems to be without influence on its viscosity, as might be expected from such a superficial, easily reversible treatment.

F. C. VAN HEURN (Meded. Rijksvoorlichtingsdienst voor den Rubberhandel, Delft, 2nd series (1916), page 451) found stretching and releasing the raw rubber to be without influence on the viscosity.

The effect of drying the rubber, which may cause a marked increase in viscosity (see § 233, page 571) is perhaps of a similar nature, though in this case also the vulcanising properties have not yet been investigated.

A typical example of this class is furnished by moderate heating of the rubber, which causes a decrease in viscosity but leaves the properties after vulcanisation unchanged, probably because vulcanisation itself is accompanied by a stronger effect in this direction.

G. BERNSTEIN (Z. Koll. 12 (1913), 193) found that heating the raw rubber in the absence of air decreased the viscosity markedly, and that for Hevea-rubber the decrease was most rapid between 60 and 70° C.

F. C. VAN HEURN (Comm. Delft IV, page 117) found heating 1 or 3 hours at 80° in the air to cause a relatively small decrease in viscosity. See further § 125, 145 and 165.

Heating the rubber solution, even in complete absence of air (so that no oxydation can take place) also gives a marked decrease in viscosity, the larger, the longer the time of heating.

See R. GAUNT (J. S. Ch. I. 33 (1914), 450; also I. R. J. 47 (1914), 1094) who in addition compared the decreases for different types of rubber, and for one rubber in different solvents.

PH. SCHIDROWITZ (Rubber, page 162) found an increase in viscosity after heating the solution of a sample of rubber from a 30 year old Ceylon Hevea and of an old poor sample of Fine Para for two hours on a waterbath, but most other samples showed a decrease on heating. See also PH. SCHIDROWITZ and H. A. GOLDSBROUGH, Rubb. Ind. 1911, page 260.

A. VAN ROSSEM (Rubb. Ind. 1914, page 149) found that the depolymerisation of a rubber solution, heated to 130° C, proceeded more rapidly in the presence of oxygen than of other gases (carbon dioxide, hydrogen, nitrogen), without it being possible to detect an absorption of the oxygen, which apparently acted as a catalyst.

Whether the effect of strong daylight, which decreases the viscosity of a rubber solution in benzene, also belongs to this class, is not yet known, the rubber from such a solution not yet having been tested after vulcanisation.

Direct sunlight causes the viscosity to decrease to very low values, but at the same time deteriorates the properties after vulcanisation (see § 164).

G. BERNSTEIN (Z. Koll. 12 (1913), 194) measured the viscosity of xylol solutions which had been exposed for different lengths of time to the light of a quartz lamp. The viscosity of different types of rubber finally reached the same low value in each case. What has been the effect of the ultraviolet rays on the vulcanising properties of rubber recovered from such solutions is not yet known.

On the influence of light on the viscosity of solutions see also § 233, page 572.

It is interesting to mention that the viscosity of a rubber solution, obtained by shaking the latex with benzene and so avoiding all the operations ordinarily accompanying preparation, is approximately the same as and certainly not lower than that of ordinary rubber, obtained by coagulation, so that coagulation is not accompanied by a polymerisation or similar process, which causes a higher viscosity.

F. C. VAN HEURN, Comm. Delft I, page 13.

The *second* group of factors are the chemicals which affect both rate of cure and viscosity. In vulcanisation they act as catalysers, while their effect on viscosity can be sufficiently explained by the change they cause in the solvent, as has already been discussed in the foregoing paragraph and in § 232 (page 570).

About the influence of the non-rubber substances in the rubber relatively little is known. The natural accelerator may be assumed to increase viscosity, as all processes in which such an accelerator is formed result in an increased rate of cure and viscosity.

The effect of the resins is not yet sufficiently investigated, and about the other by-substances nothing is known, these not yet having been isolated and identified chemically.

H. P. STEVENS (I. R. J. 46 (1913), 345) found the resins, obtained by evaporation of the acetone-extract of rubber, to decrease the viscosity of ordinary, resin-containing rubber a little.

PH. SCHIDROWITZ (Rubber, page 163) found that deresination caused an increase in viscosity in most types of rubber (Funtumia, Ficus and others), but a decrease in a smoked plantation-sample, the explanation being that probably in the latter case the effect of heating during the extraction of the resins was greater than the increase due to deresination.

Under the *third* head may be grouped the factors that cause a deterioration in tensile strength and a change in slope. As we discussed in § 201, a decrease in tensile strength is probably caused either by the presence of another rubber-hydrocarbon (be it a chemically different one, or only one differing in state of polymerisation) or by some

kind of decomposition or oxydation. What the intrinsic changes are that cause the differences in slope is not yet known; but they certainly are also of a deeper going nature than those brought under the above first head, which leave the slope unaltered and only affect viscosity. In § 235 we saw that such deterioration, as well in tensile strength as in slope, is probably always accompanied by a decrease in viscosity. To these cases may be added the over-mastication treated in § 211, while ultraviolet rays also depolymerise the rubber.

See the review on depolymerisation of rubber by A. VAN ROSSEM, Comm. Delft IV, page, 112.

§ 237. Use of viscosity determinations in testing.

To allow of a comparison we have depicted in Fig. 28 the viscosity of 1794 samples of different grades tested during the years 1917—1919. The average and normal values are:

	Average	Normal values
Smoked sheet	31.6	26—43
First quality crepe	30.9	26—43
Lower grades	25.8 ⁵	15—35

Values up to 65 or 75 may be obtained in some cases, whilst matured rubber may show very high figures, such as 80 or even 100. Inferior lower grades show a viscosity of only 10—15, and in cases of severe deterioration the figure may diminish to 7 or even 2 units (compare § 163 and 164, § 169 pages 363 and 365, and § 183).

Whether viscosity determinations in dilute solution are of any direct use in judging rubber, for instance for the making of cements or solutions, is not yet ascertained; the relation, if existing, will probably be complicated, because the rubber in such applications mostly first undergoes severe treatment (mastication, heating), which affects viscosity, and further because the traces of chemicals, which have a rather large

influence on the viscosity in dilute solution, have perhaps not the same effect in such concentrated, specially prepared solutions.

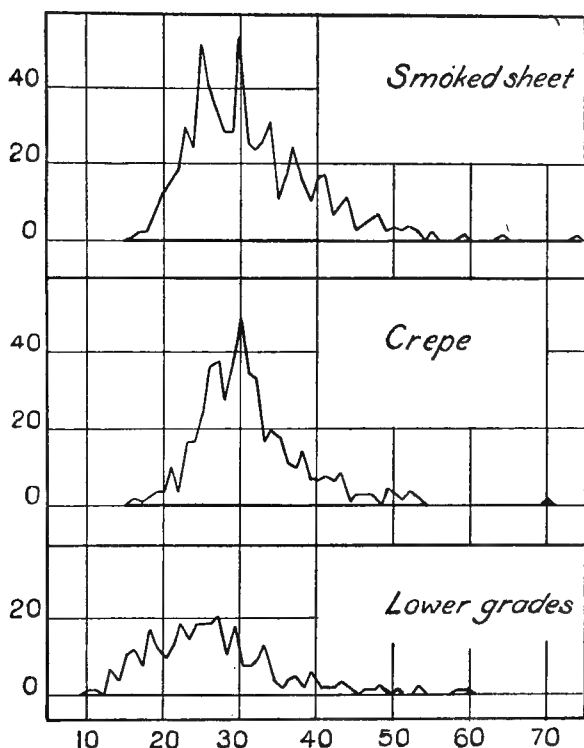


Fig. 28.
Viscosity of a large number of estate-samples
tested during the years 1917—1919.

Combined with vulcanisation testing viscosity determinations are, however, very useful. Of the many cases enumerated in § 235 a number seldom or never occur in actual estate-practice; in the choice between the remaining factors, affecting the properties or uniformity of the rubber, viscosity determinations may be of much help.

We already mentioned in § 39 (page 81) and § 119 how a normal viscosity, accompanying a low tensile strength, is a strong indication that the latter was not caused by any real deterioration but by particles of dirt. In the same way, for lower grades, a very low tensile strength with a normal

viscosity may indicate that the crepe has not been sufficiently washed and cleaned. In Fig. 27 (page 586) point 594 B indicates such a sample of lump-rubber with a low tensile strength (1.15 KG), but a high viscosity ($1.84 = 47$). In fact, washing and recrepeing this rubber had the effect of improving the tensile strength, a quite normal figure of 1.31 then being reached, while the viscosity remained the same (see 594 Bw in Fig. 27).

As regards differences in rate of cure, the accompanying change in viscosity may mostly indicate in which direction the cause must be sought. When viscosity decreases or increases at the same time as rate of cure, then some factor in preparation has mostly played a role; when the rate of cure increases, but viscosity decreases, then the taking into tapping of young divisions, or the application of a heavier tapping system may be suspected. For one who is in a position by a personal visit to check the results of the tests with the actual state of affairs on the estate such indications are, of course, very helpful.

That viscosity determinations alone are of little value in judging plantation-rubber and controlling methods of preparation on estates, will be clear from the foregoing. Viscosity is too easily affected and influenced by too many factors, so that conclusions as to the causal factor would not be possible. Even when regularly testing the rubber of one estate, the viscosity determination is not a sufficient gauge, as equal values for viscosity do not mean that the rate of cure also remained the same, and as a rather variable viscosity need not be an indication of a lack of uniformity in vulcanising properties.

See for instance the examples on pages 330 and 331, and further O. DE VRIES, Arch. 2 (1918), 471 and 472; O. DE VRIES and W. SPOON, Arch. 3 (1919), 257—265.

That viscosity, in general, is no indication as to quality, can easily be demonstrated by two examples. The first clot obtained by partial coagulation may show a very high viscosity, but its composition and properties after vulcanisation stamp it as a second grade rubber (§ 176). On the other hand

rubber prepared after the Brazilian method or after the Kerbosch-process may show a low viscosity, though the properties after vulcanisation are in no way inferior.

H. W. WOUDESTRA (Z. Koll. 5 (1909), 31) proposed viscosity determinations in an Ostwald viscosimeter for the evaluation of rubber.

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (Rubb. Ind. 1911, page 261; compare SCHIDROWITZ, Rubber, page 165 and Z. Koll. 12 (1913), 254) hold viscosity figures, within one botanical species, to give a direct line as to strength, general condition and vulcanising capacity, and found the estimation of viscosity of extreme and practical value when numerous samples have to be compared rapidly.

CL. BEADLE and H. P. STEVENS (I. R. J. 48 (1914), 530) in a large number of samples found no relation between the viscosity of dilute or more concentrated solutions and the properties after vulcanisation.

§ 238. Other physical properties of raw rubber.

While the physical properties of vulcanised rubber are of such prime importance in the use of rubber articles, relatively little is known as to how far the physical properties of the raw product play a role in manufacture. After what we said in § 105 and 230 it need not be repeated that the physical properties have perhaps a more direct importance for the preliminary treatment of the raw rubber in manufacture (masticating, mixing etc.) or for special uses (solution etc.); the physical properties of the vulcanised article may differ from those of the raw product because of the large influence of vulcanisation and of the compounding ingredients.

Still it is not saying too much to say that the physical properties of raw rubber have been somewhat neglected. Though valuable data in a general sense have been collected, methods of testing that are of importance for manufacturers have not yet been made known, and there is no indication as to how far the determination of different physical properties might be a help in judging raw rubber.

As so little can be said about the influence of the composition of the latex, the preparation of the rubber

and other factors on the physical properties of the raw rubber, we need not here discuss what has been done in this field.

Even for such a simple property as specific gravity no accurate data are available. Figures between 0.91 and 0.93 or even higher are mentioned in literature, but whether the method of preparation (milling, blocking etc.) influences the specific gravity of raw rubber has not yet been investigated.

The fundamental studies of H. BOUASSE were already mentioned in § 230; on the thermal effects in rubber see, for instance, A. SCHWARTZ and PH. KEMP, C. Gp. 1911, page 5293 and G. Ztg. 25 (1911), 1853; on the dilatation see H. BOUASSE, C. Gp. 1911, 5286, and J. H. POYNTING, I. R. J. 46 (1913), 616. All these and similar investigations treat rubber as an elastic substance in comparison with other materials, but do not descend into details about the different types of rubber or of the practical significance of these physical properties.

A method of GERBER for determining the plasticity of raw rubber (by the time that a loaded pin takes to penetrate 1 mm into a pressed block at 100°) is described in Bull. I. Ch. 14 (1911), 943, also C. Gp. 1912, page 6312.

CHAPTER XXI.

CHEMICAL COMPOSITION OF RUBBER.

§ 239. Chemical composition of rubber and its importance in testing.

The chemical composition of Hevea-rubber of the ordinary types varies so little that, in testing rubber, a chemical analysis is seldom necessary. Determinations of the moisture content are sometimes asked for, as the market is inclined to ascribe a certain kind of stickiness to moistness (see § 121 and 241). In other cases a chemical analysis may sometimes serve to corroborate conclusions drawn from other sources, but the chemical analysis of Hevea-rubber only leads to really significant results when special types (rubbers prepared by special methods, see f.i. Chapter XV) are to be tested, or when a statement is asked for as to whether a certain rubber is derived from Hevea and not from *Manihot*, *Castilloa*, *Ficus* or other species.

The chemical composition of first quality Hevea-rubber (sheet or crepe) is approximately as follows:

Caoutchouc-hydrocarbon	92 — 94 %
Moisture	0.3 — 1.2 %
Mineral substances (ash)	0.15 — 0.5 %
Acetone soluble matter (resins etc.)	2.5 — 3.2 %
Nitrogenous matter (proteins etc.)	2.5 — 3.5 %

Investigations of the composition of rubber are much more numerous and have been pushed much farther than those regarding latex or serum; but owing to the complex colloidal nature of the hydrocarbon itself and of some of the other constituents of rubber, and further owing to the very small amount in which some by-substances are present, our knowledge is still very far from complete.

We do not intend to give a review of all that is known about the composition of rubber, but restrict ourselves to a brief summary of the principal points, with a special view to the relation between composition and preparation and between composition and properties of the rubber which were treated in the foregoing pages.

We may add that our data on chemical analysis, published in different chapters of this book, have always been determined by the methods indicated by the Government Institute at Delft, Holland (see Comm. Delft Part II).

§ 240. Rubber-hydrocarbon.

The complex nature of the rubber-hydrocarbon, and the special difficulties offered by its typical colloidal character, have brought it about that, despite many elaborate and brilliant investigations, its properties are not yet completely known. That its composition is $(C_5H_8)_n$, and that it is an isoprene-derivative, has been proved in many ways, and many chemical derivatives have been prepared. But in how far the chemical composition of the hydrocarbon and its state of polymerisation or aggregation affect the properties of the rubber, such as tensile strength and rate of cure, still remains to be investigated; and whether the hydrocarbon from young and old trees, from the young twigs or the stem, is chemically and physically speaking the same or not, is also unknown.

In this book we will not discuss the large experimental material, gathered to clear up the composition of the hydrocarbon, as the relations between the structure of the hydrocarbon and the preparation and properties of plantation-rubber are as yet wholly unknown.

The reader will find a review of the principal data on this point in C. HARRIES' book „Untersuchungen über die natürlichen und künstlichen Kautschukarte“, Berlin 1919; see further A. TSCHIRCH, Schweiz. Chem. Ztg. 1919, page 153, I. R. J. 58 (1919), 789, and others

§ 241. Moisture.

Rubber unavoidably contains a certain amount of moisture. Even when freed completely from it by drying at higher

temperatures, it again absorbs moisture from the air after cooling, and if nothing is changed it will regain the same state of equilibrium as before.

This state of equilibrium is dependent upon two factors:

- 1) the moisture-content and temperature of the surrounding atmosphere;
- 2) the properties (composition) of the rubber.

Influence of the atmosphere.

The higher the moisture-content of the surrounding atmosphere, the more water the rubber absorbs. The higher the temperature of a certain volume of air, the more water the rubber gives off, because by heating the air becomes relatively drier. But in atmospheres of the same percentage moisture-content, the rubber seems to retain more moisture at higher temperatures.

This point was studied by Miss KRAYENHOFF VAN DE LEUR (Comm. Delft II, page 41). By placing pieces of rubber above dilute sulphuric acid of different concentrations, giving atmospheres of 49, 77, 89 and 100 % of moisture, and comparing temperatures of 16° and 30° C, she concluded that the moisture-content of sheet and crepe increases with increasing moisture-content of the atmosphere, and very rapidly so for atmospheres with more than 85 % of moisture, and that at 30° the moisture-content of the rubber is higher than in an atmosphere of the same moisture-content at 16° C. The figures for the percentage of moisture in the rubber were:

% Moisture of the air	Sheet		Crepe	
	16°	30°	16°	30°
100	1.85	2.88	2.80	4.54
89	0.88	0.76	0.89	1.06
77	0.31	0.44	0.39	0.37
49	0.23	0.24	—	—

These figures give a good idea of the differences in moisture-content of the rubber from changes in the condition of the atmosphere. For general conclusions more data would be desirable.

The exact influence of both factors, temperature and moisture-content of the atmosphere, is not yet known, and insufficient data are as yet available especially on the question whether under ordinary atmospheric conditions in the tropics rubber always contains more moisture than under European conditions, so that a loss in weight during transport from the East to Northern countries is unavoidable.

A difference between plantation-weight and market-weight is often found, amounting up to 1 %. But several other factors may here play a role, such as loss in weight of the tare, actual losses in rubber, differences in the weighing scales and so on.

As crepe-rubber in the East contains on the average 0.6 % of moisture, and smoked sheet 0.8 % (see below), and both grades in Europe still contain a certain degree of moisture, the loss in moisture cannot amount to more than a few tenths of one percent, and the higher figures sometimes assumed for it are unfounded.

As exact data for the loss in moisture during transportation over sea still fail, it is interesting to compare the average figures for a large number of samples tested in Java and in Holland, which, though they do not relate to the same samples, give a general idea as to the moisture-content in the wet tropical West-Java climate and under European conditions:

	Holland		Java	
	Average	Normal figures	Average	Normal figures
Pale crepe . .	0.42	0.18—0.90	0.6	0.35—1.0
Smoked sheet .	0.61	0.30—1.08	0.8	0.45—1.1

See Comm. Delft II, page 40 and Arch. 2 (1918), 53 and 858.

The figures, as also in the following pages, represent the „loss in weight by heating at 95° C to constant weight“. Besides water, traces of other volatile substances may be included, and in the case of smoked sheet the loss of volatile smoke-constituents may be of some importance. See the warning on this subject by F. KAYE (I. R. J. 40 (1910), 903).

From these figures a decrease in moisture-content of only 0.2 % during transport to cooler climates would appear to be the most probable.

In investigations of this kind it should not be forgotten that rubber is not a stable product. Especially the hygroscopic components gradually seem to undergo a change, be it a decomposition or oxydation, or only a drying up (pectisation) of gelatinous substances, by which the gel loses in absorptive power. The fact is that hygroscopic rubber (see f.i. § 172 on greasiness), on keeping, loses its stickiness and becomes more and more dry. Exact investigations on this point however still fail.

The „loss on washing“, in which water-soluble rubber constituents may be inclosed, is of course quite another figure, though often it may nearly coincide with the loss at 95°.

The differences in moisture-content during the dry and wet monsoons in the East are also small; from a large series of determinations in ordinary estate-samples during a wet and a dry period the following figures were found:

	Average		Normal limits		Highest values	
	wet	dry	wet	dry	wet	dry
Pale crepe	.67	0.59	0.34—1.01	0.39—0.71	1.37	0.95
Smoked sheet	0.76	0.87	0.43—1.07	0.52—1.10	1.38	1.20

See O. DE VRIES, Arch. 2 (1918), 852.

The differences are smaller than one would expect; the only marked feature is that during the dry monsoon the very high figures do not occur.

Whilst the above average figures do not show large differences, the influence of the condition of the atmosphere is distinct when testing one and the same sample early in the morning and during the hot hours of midday. The moisture-content may diminish by 0.3 or even 0.8 %, to increase again in the evening and during the night.

G. S. WHITBY (J. S. Ch. I. 37 (1918), 278 T) for free hanging pieces of crepe found the moisture-content to vary between 0.10 and 0.53% or between 0.19 and 0.71%; the variations for a piece of sheet were smaller (between 0.25 and 0.36%).

F. C. VAN HEURN (Arch. 2 (1918), 25, 41 and 115) for free hanging pieces of crepe found daily variations in moisture-content from 0.25 to 0.55% and on a wetter place from 0.4 to 0.65%; for smoked sheet it oscillated between 0.2 and 1.0%.

Similarly, a sample analysed after a few wet days may show a markedly higher moisture-content than when it is retested after some dry days; a decrease of 0.2 to 0.4% in moisture-content in such cases is not uncommon.

See O. DE VRIES, Arch. 2 (1918), 47 and 53.

From these data it will be clear that the moisture-content of rubber, sampled under changing atmospheric conditions, is not a fixed, but an accidental figure. In testing rubber for moisture-content, the only point of importance is whether the figure lies between the normal limits; the figure actually found, being of an accidental nature, allows of no further conclusions.

Compare F. C. VAN HEURN, Arch. 2 (1918), 44 and 115.

Whether a figure for „hygroscopicity” (moisture-content under fixed conditions, f.i. equilibrium reached in the atmosphere above a certain salt-solution, or above sulphuric acid of a certain dilution) has any value in testing rubber, remains to be investigated.

Influence of the composition of the rubber.

The second factor mentioned above, the composition of the rubber, is of more importance and is the cause of large variations.

Rubber derives its absorptive power for water, at least for a great part, from the non-rubber constituents, among which are hygroscopic substances; the more of them the rubber contains, the more hygroscopic it will be, and it is not astonishing that the method of preparation has an influence upon the moisture-content of the air-dry rubber.

As an example it may be mentioned that rubber from undiluted latex shows a higher moisture-content (say 0.2%)

more) than rubber from diluted latex, which (see § 64) contains less serum-substances.

Rolling the rubber shortly after coagulation gives a more hygroscopic product than rolling the next day, as during the night part of the hygroscopic products is decomposed (or pectised?). For crepe the difference is approximately 0.1 %, for sheet it may amount to 1 %, though on the average it is perhaps only 0.3 %. Sheets that are rolled shortly after coagulation and not washed with or soaked in water, may even retain 2 to 3 % of moisture; they may be so hygroscopic that on wet days small drops of water are formed on the surface. This phenomenon is closely related to the defect called greasiness (see § 172). By extracting part of the serum-substances (f. i. soaking or keeping overnight in water) the resulting rubber is drier; and the moisture-content in sheet, after prolonged extraction, may even decrease to 0.2 %.

The use of chemicals in preparation may also have an influence on the moisture-content; for instance crepe prepared with bisulphite contains on the average 0.1 % of moisture more than when no bisulphite is used.

Figures and details see O. DE VRIES, Arch. 2 1918), 858 and 378.

For the moisture-content and its daily variations (ranging from 1.44 to 3.11 %) in a sample of rubber containing the greater part of the serum-substances, see G. S. WHITBY (J. S. Ch. I. 37 (1918), 280 T).

Lower grades may show higher figures for moisture-content than first quality smoked sheet and crepe; thick crepe especially may contain up to $1\frac{1}{2}$ % of moisture, and even more, if not completely dry.

As the moisture-content is of some importance for the manufacturer, who has to dry the rubber before use, and as a high moisture-content or hygroscopicity may lead to mouldiness, development of spots and so on, the method of preparation should be so chosen that the moisture-content will be low (see for instance § 139).

On the market, perhaps especially in Eastern markets, where rather fresh rubber is handled, complaints are sometimes heard that a certain crepe is „wet”, whilst the moisture-content is quite normal. The cause is often a certain degree of stickiness caused by rolling the crepe too thin (compare § 121).

§ 242. Mineral substances.

Mineral substances, determined as ash after incinerating the rubber, are found in ordinary plantation-rubber to an amount of between 0.15 and 0.5 %.

G. VERNET (Bull. I. Ch. 14 (1911), 925; C. Gp. 1912, page 5965) gives the average ash-content of pale crepe as 0.5 %, of biscuits or sheets 0.33 %; his figures (ibid. 806) range from 0.3—0.6 for crepe or sheet, and up to 2.14 % for tree-scrap.

The Imperial Institute in several publications (see f.i. Bull. Imp. Inst. 5 (1907), 247 and also ibid. page 49) found an ash-content in first grade crepe and sheet between 0.14 and 0.48 %; in numerous other analyses the figures varied generally from 0.2 to 0.5 %. For plain sheets prepared after standard method (Bull. Ceyl. 27, page 15; Bull. Imp. Inst. 14 (1916), 498 and 562) the ash-content varied from 0.15 to 0.31 with an average of 0.235 %.

The Government Institute at Delft (Comm. Delft II, page 52) found for smoked sheet an average figure of 0.38 %, and for crepe 0.30 %; the figures for the majority of samples lay between 0.15 and 0.55 %.

Types of rubber prepared by methods other than acetic acid coagulation may show a much larger ash-content. The figures given in different chapters may be summarized as follows:

	Ash-content in rubber
Coagulation by heating the latex (see § 100)	0.3—0.7 %
Coagulation by total evaporation of the latex (see § 102 and 193)	1.5— 2 %
Brazilian method (see § 189)	0.6 %
Electrical coagulation (§ 194)	0.4—1.0 %

In the lower grades, especially in the bark- and earth-rubbers, the ash-content may be found to be much higher because of included impurities (particles of soil etc.). The

figure for such cases may give an indication as to the cleanness of these rubbers, whilst microscopic examination of the ash may deliver the proof that particles of dirt are present.

The average figures from series of determinations made by A. J. ULTÉE (Arch. 3 (1919), 417) are:

Light brown tree-scrap	0.51 % ash
Dark brown tree-scrap	0.68 % "
Bark-rubber	0.80 % "
Earth-rubber	2.22 % "

whilst the figure for earth-rubber, after better washing in a Universal machine, decreased to 1.46 % (see § 183 and 185). In samples of brown crepe an ash-content of 1.7 % and even 4.0 % was found in the Imperial Institute (Bull. Imp. Inst. 11 (1913), 377).

The content of mineral matter in first grade rubber varies to some extent with the composition of the latex. After opening a tapping cut on trees that had had a period of rest the ash-content of crepe from undiluted latex may for instance in some weeks increase from 0.25 to 0.40, and for crepe from 15 % latex from 0.15 to 0.25 % (see § 29).

Heavy tapping also, which causes a higher ash-content in the latex, and a much higher figure when the ash is calculated on rubber or total solids (see § 32), gives a rubber with a higher ash-content. For ordinary tapping systems the figure may increase from 0.16 % to 0.26 %.

The ash-content of rubber is further to a marked extent dependent upon the method of preparation. Ordinary acetic acid coagulation from undiluted latex gives an ash-content of 0.3 to 0.35, against 0.2 to 0.25 when the latex is diluted to 15 %, and 0.15 for rubber from strongly diluted latex (§ 64).

Coagulation with sulphuric acid seems to give a somewhat lower ash-content than acetic acid (see § 86), whilst alcohol as a coagulant gives a decidedly higher ash-content (0.4 to 0.45 against 0.3, see § 99), and coagulants such as alum may increase the ash-content to 0.6 or even 1.0 % (§ 88).

In § 157 we mentioned some figures indicating that sheet-rubber may have a somewhat higher ash-content than

crepe. This ash-content may even be twice as large in sheet, when no soaking in water takes place. For instance:

	Crepe	Sheet
From undiluted latex	0.28	0.57
From 15 % „	0.22	0.39

Our knowledge about the constituents of the ash is still far from complete. Probably the same bases and acids are present as in latex (see § 4), perhaps with a somewhat increased amount of iron, incorporated during preparation; but the ratio of the different components, and the influence of the method of preparation on the composition of the ash are as yet unknown.

C. O. WEBER (Ind. Rubb., page 12) mentions as bases only lime, magnesia, alumina and iron, of which lime predominates.

Phosphoric acid forms approximately $\frac{1}{4}$ of the ash of rubber; F. KAYE (Rubb. Ind. 1914, page 139) gives the following figures for dry rubber:

	Ash	P ₂ O ₅	P ₂ O ₅ in ash
Pale crepe	0.17 %	0.035 %	20½ %
Smoked sheet (unwashed) . .	0.312 „	0.092 „	29½ „
Byrne cured rubber (unwashed) .	0.555 „	0.162 „	29 „

As to the influence of the mineral-constituents on the properties of the rubber very little is known. A certain amount of them remains absorbed even after the most thorough washing or extraction, as was to be expected from a colloid such as rubber; but whether such traces of mineral constituents play any role in vulcanisation is yet unknown. Probably the influence is not great, as the addition of different salts to the latex prior to coagulation has no large influence on the vulcanising properties of the rubber (see Chapters III and VI).

Sodium salts were found to increase the rate of cure somewhat, when added in the form of salts of volatile acids (sulphite, carbonate, bisulphite), so that sodium acetate is formed during coagulation (see § 44, 45, 48 and 52). On the other hand sodium chloride, when added in rather large quantities to the latex, retards the rate of cure (see § 40), whilst sodium sulphate seems to be without influence (§ 52).

Calcium chloride, added in small quantities to the latex, has no influence on the properties of the rubber (see § 97); about the influence of larger quantities no data are as yet available.

A. VAN ROSSEM (Comm. Delft VI, page 199) found that no correlation exists between the ash-content of raw rubber and its rate of cure.

In testing Hevea-rubber the figures for ash-content do not give any direct indication as to quality, but may be of considerable help in special cases. So, for instance, when suspecting coagulation with alum, a high figure for ash combined with a small rate of cure may give a strong indication. Special methods (such as evaporation of latex and the like) are also easily recognised by a chemical analysis, including the ash-content.

In this connection it is worth while to repeat that it is as a rule not possible to detect, for instance, the use of sodium bisulphite (see § 48) by an analysis of the ash. The amount of bisulphite generally used — 1 ‰ of the latex, or some 2—3 ‰ of the rubber — is small and, of course, a large part of the soluble products formed from it (sodium sulphate and acetate) remain in the serum. Only excessive amounts of bisulphite can be traced in the ash of rubber.

§ 243. Watery extract.

The water-soluble constituents may be determined by extracting the finely cut rubber with water, and this figure may be of importance in rubber testing, as the watery extract will be larger, when methods of preparation have been followed that leave more than the ordinary content of serum-substances in the rubber.

In the watery extract are found a part of the mineral matter, some nitrogenous matter, whilst quebrachite, when present in the rubber, will also find its way into this extract. Details about the components of the watery extract are however still very scarce.

The solids in the watery extract of ordinary plantation-rubber amount to about 0.5% (calc. on the rubber) and in some cases up to 1%.

See Comm. Delft II, page 66.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. (1912) 25, page 583, see also G. Ztg. 27 (1913), 1907) mention a water-extract for crepe of 0.4 to 0.5 % and for smoked sheet of 1.0 to 1.5 %. They further determined how much of the acetone-extract of certain rubbers is soluble in water, and also the amount of watery extract of the acetone-extracted rubber, besides the watery extract of the original rubber. They found that acetone does not extract the whole of the water-soluble substances; and that in some cases the water-soluble substances from the acetone-extract and those from the acetone-extracted rubber, taken together, give a higher figure than the watery extract of the same rubber.

P. DEKKER (Comm. Delft I, page 26) made some similar investigations with rubber obtained by evaporation of preserved latex, and with rubber from dialysed latex; in the latter case the acetone-extract contained no water-soluble substances. The watery extract of a rubber prepared by evaporation, amounting to 5.7 %, contained 1.0 % ash and 1.3 % protein, so that 3.4 % were formed by other substances, amongst which probably quebrachite.

DEKKER showed furthermore (ibid. II, page 55) that the watery extract from ordinary rubber contains nitrogen-compounds.

The method of preparation has a distinct influence on the watery extract of the rubber. As far as the ordinary method of preparation goes, the largest differences are perhaps found between crepe, that is thoroughly washed during preparation, and sheet, if not soaked in water after milling. For example :

	Crepe	Sheet
From undiluted latex . . .	0.4—0.45	1.2—2.0
From 15% „ . . .	0.2—0.25	0.6—1.1

The influence of diluting the latex may at the same time be seen from the above figures.

The coagulant may also give a difference in this respect; for instance, sulphuric acid was found to give a somewhat lower watery extract (see § 86). After spontaneous coagulation the watery extract is the same as in crepe from undiluted latex, coagulated by acetic acid; but processes such as the Ilcken-Down method (see § 195) give a higher watery extract.

In § 102 we have already mentioned that rubber obtained by evaporation of the latex, which contains 10 to 12% substances which otherwise remain in the serum, only gives a watery extract of some 5%, so that half of the serum-constituents have become insoluble, or are too strongly absorbed by the rubber.

The influence on the properties of the rubber of the water-soluble substances from the serum that are incorporated in rubber obtained by evaporation of the latex, was treated in § 102 and 112. These substances accelerate vulcanisation, but leave the other properties unchanged.

As to the influence of the much smaller amount of substances that form the ordinary watery extract of sheet and crepe, very little is known. The effect of soaking the sheet some hours in water, viz. to retard the rate of cure markedly (see § 139) would seem to indicate that extracting ordinary rubber with water removes an accelerator. Comparative figures for rubbers fully extracted with water and untreated controls, in experiments with different methods of preparation, are not yet to hand, so that the influence of the extractable substances is not yet known in details.

§ 244. Acidity.

Different types of rubber, when extracted with water, give an acid extract. The proof that this acidity is partly or wholly caused by acetic, lactic or one of the other acids that play a role in coagulation, has not yet been delivered; decomposition-products formed by hydrolysis of the non-rubber constituents perhaps also play a role.

See F. KAYE, I. R. J. 45 (1913), 1297.

In judging the figures found in literature it should, of course, be taken into account that the amount of acid found

after extraction will depend upon the amount of water used, the duration of the extraction, the temperature (cold or boiling water) etc. Methods used by different investigators have varied considerably.

In general the acidity of sheet-rubber is 5 times or more higher than that of crepe, whilst the lower grades may also show higher figures.

The acidity of raw rubber attracted special attention in the early years of plantation-rubber, when a harmful influence of coagulation with acid was feared. It was, however, soon found that plantation-crepe showed a lower acidity than Brazilian smoked balls (see also § 186).

The acidity is generally calculated as acetic acid on dry rubber.

CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 1257) found an acidity of 0.02 to 0.12 for pale crepe, and 0.15 to 0.29 for sheet-rubber, against 0.12 to 0.17 for Para samples, and argued that the fear of the supposed acidity of plantation-rubber was unfounded.

The same authors (I. R. J. 46 (1913), 164) find the usual limits to be:

Smoked sheet	0.10 — 0.20 %
Unsmoked sheet	0.05 — 0.15 %
Pale crepe	nil — 0.10 %
Fine hard Para	0.10 — 0.20 %

D. SPENCE (Biochem. Journ. 3 (1908), 168; I. R. J. 41 (1911), 94) mentions that he found the watery extract of plantation-rubber acid, but that of Brazilian balls to be alkaline. This last fact was refuted by CL. BEADLE and H. P. STEVENS (I. R. J. 41 (1911), 1257), who pointed out that rubber coagulated with smoke must be acid.

The latter results were confirmed by PH. SCHIDROWITZ (I. R. J. 41 (1911), 1324), who stated that there is no relationship between the acidity of raw rubber and its quality.

PH. SCHIDROWITZ and H. A. GOLDSBROUGH (I. R. J. 44 (1912), 1147), in samples of unsmoked sheet prepared by G. S. WHITBY, found an acidity of 0.01 to 0.055 %; the acidity was higher, when more acid was used in coagulation.

F. KAYE (I. R. J. 45 (1913), 1297) found an acidity in crepe of 0.015 %, in dark smoked sheet of 0.029 %, in Fine Hard Para of 0.40 %.

B. J. EATON (Bull. F. M. S. No. 17 (1912), 47) found the acidity of smoked sheet 0.07 % to 0.15 %, of unsmoked sheet 0.03 % to 0.06 %, and of crepe 0.01 % to 0.015 %.

S. MORGAN (Prep. Pl. Rubber, page 235) found the acidity

of pale crepe to be 0.03 %—0.06 %, of lower grades (lump, scrap etc.) to reach 0.07 % to 0.12 %, of unsmoked sheet 0.05 % to 0.19 %, and of smoked sheet 0.08 % to 0.32 %, so that only the latter grade reached the figure for Fine Hard Para (0.24 % to 0.31 %), especially when it was heavily smoked.

The Government Institute at Delft (Comm. Delft II, 68) gives the following figures for the acidity of ordinary plantation-rubber, calculated as acetic acid on the dry rubber:

	Crepe	Sheet
Average.	0.006 %	0.03 %
Highest	0.024 %	0.08 %
Lowest	0.006 %	0.006 %

A. VAN ROSSEM (Comm. Delft VI, page 199) found that no correlation exists between the acidity of raw rubber and its rate of cure.

Of course acidity in raw rubber is quite another thing to the formation of acid in vulcanised rubber on keeping, which accompanies its deterioration (see H. L. TERRY, J. S. Ch. I. 31 (1912), 1104; B. J. EATON and F. W. F. DAY, J. S. Ch. I. 38 (1919), 339 T).

Rubber prepared by special processes often shows a higher acidity. In § 186 we already remarked that Fine Hard Para generally shows the acidity of plantation-sheet, as also appears from the figures given above. When all or nearly all the serum-substances are retained, a much higher acidity may, however, result. For instance rubber prepared after the Kerbosch-process may show an acidity of three times that of sheets.

Comm. Delft II, page 68.

Whether deterioration by micro-organisms, causing spots (§ 167) or mouldiness (§ 171), increases the acidity of the rubber, remains to be investigated. Formation of acids may also be postulated in rubber showing real tackiness by oxydation, but has not yet been proved.

On acids formed by oxydation of rubber see S. J. PEACHEY and M. LEON (J. S. Ch. I. 37 (1917), 55; also I. R. J. 54 (1917), 850).

The acidity of spontaneously coagulated rubber (during the formation of which, as we have seen in § 94—97, the latex shows a higher acidity than in normal acetic acid coagulation) has not yet been compared with that of ordinary rubber, neither are data available as to an eventual acid formation during processes such as maturation.

§ 245. Components soluble in acetone.

The acetone extract plays an important role in rubber testing, partly because it is used in determining the coefficient of vulcanisation, partly because the resin-content of the so-called „wild” rubbers forms one of their most prominent characteristics. In first grade Hevea-rubber, as mentioned above, the resin-content shows only relatively small variations; the acetone extract is generally found between 2.5 and 3.2 % of the dry rubber.

G. VERNET (Bull. I. Ch. 14 (1911), 806) gives figures of 1.3—4.5 % of „resins soluble in acetone” for crepe or sheet, and holds that the method of preparation has a decided influence on the resin content.

Experiments in Ceylon (Bull. Ceyl. 27, 15; Bull. Imp. Inst. 14 (1916), 562) gave in samples of sheet-rubber a resin-content between 2.30 and 3.47, on the average 2.88 %. The analyses of the Imperial Institute gave mostly figures between 2.0 and 3.5 %; the values in an older series of observations (Bull. Imp. Inst. 5 (1907), 49 and 247) lay between 1.64 and 3.58 % for crepe and sheet. In a brown smoky biscuit 4.3 % acetone extract were found (Bull. Imp. Inst. 11 (1913), 378), whilst in other cases (Bull. Imp. Inst. 8 (1910), 343 and 13 (1915), 19) figures up to 4.9 % were reached.

The Delft Institute (Comm. Delft II, page 48) found the acetone-extract in a series of crepe-samples to be on the average 2.88 %, in smoked sheet 2.89 %.

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 25, page 582; see also G. Ztg. 27 (1913), 1907) mention figures of 1 to 3½ % for sheet and crepe with an average of about 2.5 %.

H. P. STEVENS (I. R. J. 46 (1913), 345) gave figures for the acetone extract of different fractions obtained by successive treatment of the rubber with benzene.

The acetone extract, besides substances that belong to the group „resins”, also contains some of the components that are soluble in water (which resins are not) and some

nitrogenous matter (resins are nitrogen-free). What is generally called „resins”, and in reality is the whole of the acetone-soluble matter, is therefore (and perhaps still more so than the other arbitrary groups as proteins, ash, water-soluble substances) a rather complex mixture of different substances which are only very imperfectly known, and from which the single constituents are seldom distinguished or determined separately.

We will not here give a review of all data available on the acetone-soluble substances. For literature on the „resins” in rubber the reader may be referred to the textbooks of A. TSCHIRCH (*Die Harze und Harzbehälter*) and G. HILLEN (*Über Kautschuk- und Guttäpercha-harze*, Bern 1913); to reviews such as by F. JACOBSON (G. Ztg. 30 (1915), 28 and 53), and others.

C. O. WEBER (*Ind. Rubb.*, page 12) already mentions the presence of mineral matter (organic salts) in the acetone extract.

CL. BEADLE and H. P. STEVENS (*VIII. Int. Congr.* 25, 581; see also G. Ztg. 27 (1913), 1907) gave some figures for the water-soluble parts in the acetone extract and in the acetone-extracted rubber. In an acetone extract of 3–4%, 0.6 to 1.5% were found to be soluble in water. The rest of the acetone extract, after extraction with water, would in all probability give a better figure for the real resin-content.

F. W. HINRICHSSEN and J. MARCUSSEN (*Z. angew.* 23 (1910), 49; *Mat. Pr.* 29 (1911), 121 and 450) determined the saponifiable part of the resins from Hevea-rubber, and found it to amount to 80–85%. They further stated that the resins from Hevea-latex, in contrast with those from *Ficus*, *Manihot*, *Castilleja* and other species, do not show any optical activity, (see also F. W. HINRICHSSEN and E. KINDSCHER, *Chem. Ztg.* 34 (1910), 230). This fact was confirmed by the Government Institute at Delft (*Comm. Delft II*, page 49).

P. DEKKER (*Comm. Delft II*, pages 46 and 55) showed the presence of nitrogenous matter (up to $\frac{1}{10}$ of the acetone extract) and of water-soluble matter in the acetone extract. He also (*l.c.* page 49) gave figures for the saponifiable part, the former constituting $\frac{1}{4}$ to $\frac{1}{2}$ of the resins.

As to the influence of factors that alter the composition of latex on the resin-content of the rubber, few data are available.

The age of the trees is said by some to influence the resin-content of the rubber; but this is not confirmed by investigations of others (see § 24).

Continued tapping after opening a cut, or heavy tapping, do not seem to influence the resin-content of the rubber (see § 29 and 32).

Of the method of coagulation and preparation, also, little influence on the acetone extract of the rubber has as yet been stated, and it would seem that this figure in Hevea-rubber is not readily changed by the ordinary factors.

As an example the following average figures may serve for crepe and unsmoked sheet prepared from the same latex:

	Crepe	Sheet
Latex undiluted, coagulum rolled same day.	3.2	3.5
" " " " next "	2.9	3.3 ⁵
Latex diluted to 15 %, coagulum rolled same day	2.9	3.1
" " " " " next "	3.1	3.1 ⁵

Tackiness caused by strong acids may result in a marked increase in acetone-soluble substances; see § 91.

The lower grades may contain much more acetone-soluble constituents than the first quality product; and when decomposition, caused by oxydation of the rubber, and resulting in tackiness, sets in, the acetone extract rapidly increases and at last, for rubber that has become semi-fluid, may reach figures as high as 80—90 %.

G. S. WHITBY (I. R. J. 45 (1913), 1043, also Z. Koll. 12 (1913), 190) mentions tacky rubbers of which 71.3 and 78.0 % were soluble in acetone. In samples prepared with a trace of copper sulphate, which had become completely tacky and weak, we found even 93 % to be soluble in acetone.

The influence of the acetone-soluble constituents on the properties of the rubber is not yet wholly cleared up. Even whether the acetone-soluble substances accelerate or retard vulcanisation, is not yet satisfactorily settled, and results are contradictory, perhaps owing to differences in

the substances that are extracted in different methods (more or less nitrogenous matter, and so on).

CL. BEADLE and H. P. STEVENS (VIII Int. Congr. 25 (1912), 581); also G. Ztg. 27 (1913), 1908) found that removal of the greater part of the resins retarded the cure, while the tensile properties of the rubber were greatly reduced; the resin-extracted rubber perished much more rapidly on keeping than unextracted samples, which deterioration was not due to the heating during extraction. Extraction of Hevea-crepe in the cold with acetone for 3½ months (removing 3.05 %) however gave on testing a curve that was further advanced, therefore a quicker curing rubber, whilst extraction with alcohol (removing 1.94 %) gave a slower curing rubber.

H. P. STEVENS (I. R. J. 47 (1914), 404; also Z. Koll. 14 (1914), 91), found that rubber extracted with acetone in the cold vulcanised more slowly, whilst addition of the extracted resins to the original (unextracted) rubber accelerated the cure somewhat. Pontianac resin and colophony did not restore vulcanisation in the same way as the acetone extract from the rubber itself—which may, perhaps, be ascribed to the nitrogen derivatives in the acetone extract (see above). In a mixture containing litharge (J. S. Ch. I. 35 (1916), 874) the acetone-extracted rubber also vulcanised more slowly and deteriorated quicker on ageing, whilst addition of the acetone extract accelerated the cure.

L. E. WEBER (VIII Int. Congr. (1912) 9, page 95) studied the influence of the resins on vulcanisation in different types of rubber. The resins often hinder vulcanisation, as they dissolve or bind the sulphur. In general a higher resin-content goes hand in hand with less satisfactory properties before and after vulcanisation. He regards the presence of resins as absolutely essential to vulcanisation, as rubber extracted with acetone „could not be vulcanised”, at least gave very poor results. H. P. STEVENS (J. S. Ch. I. 35 (1916), 875) ascribes this to the small rate of cure of such rubber.

A. VAN ROSSEM (Comm. Delft VI, page 196) found a distinctly positive correlation (though the correlation coefficient was low) between the percentage of resin and the rate of cure of 315 samples of first quality crepe and sheet.

F. C. VAN HEURN (Comm. Delft VI, page 195) found that extracting the rubber with acetone increases the rate of cure, whilst the tensile strength diminishes, which latter may be ascribed to the heat used in the extraction. Adding the solids from the acetone extract to the extracted rubber restored the former rate of cure, and adding a double quantity of them retarded the original rate of cure, so that in these experiments

the acetone-soluble substances were distinctly proved to retard the rate of cure. The contradiction with the above results of STEVENS is not yet cleared up.

In one sample of crepe, extracted with alcohol, we found an increased rate of cure, that is a decrease caused by the resins.

S. J. PEACHEY (J. S. Ch. I. 31 (1912), 1103) found that crepe extracted with acetone oxydises much more rapidly at 85° C in an atmosphere of oxygen than ordinary crepe, so that the resins present in rubber have a protective action, at least at higher temperatures.

§ 246. Nitrogenous matter.

Ordinary first grade plantation-rubber generally contains 0.3—0.55 % of nitrogen, from which by multiplying by the usual factor of 6.25 a „protein”-content of 2 to 3.5 % may be derived.

Experiments in Ceylon (Bull. Ceyl. 27, page 18; Bull. Imp. Inst. 14 (1916), 562) gave a protein-content between 2.02 and 2.68, in the average 2.32 %, in samples of sheet-rubber. The analyses of a number of samples in the Imperial Institute generally gave figures between 2 and 3.5 % for protein; a series of older analyses (Bull. Imp. Inst. 5 (1907), 49 and 247) gave figures between 1.35 and 3.18 %.

The average figure for „proteins” was found to be 2.82 % for both sheet and crepe by the Gov. Institute (Comm. Delft II, page 54), whilst CL. BEADLE and H. P. STEVENS (Z. Koll. 13 (1913), 208) mention 3.04 % as the average.

The nitrogen-content of a large number of samples, prepared in different ways, was determined by B. J. EATON, J. GRANTHAM and F.W.F. DAY (Bull. F.M.S. 27 (1918), 105), and for ordinary crepe and sheet was found mostly between 0.3 and 0.4 %.

The recalculation of the nitrogen-content, that is in reality determined, to „protein” is liable to criticism, as it is especially the simpler nitrogen derivatives, protein decomposition products such as amines and amino-acids, that in all probability play the most important role as vulcanisation accelerators. A differentiation between the several groups of nitrogen derivatives would not be out of place in the analysis of rubber; but methods of determination have not yet been developed, the chief difficulty being that the simpler nitrogen derivatives seem to be present only in very small

traces. This fact, on the other hand, justifies to a certain extent the calculating of the whole nitrogen-content as protein, and especially so when an estimate is aimed at of the rubber-hydrocarbon by indirect analysis, as the undetermined rest when the figures for the other constituents have been fixed.

That different groups of nitrogenous substances are present in rubber, has been shown amongst others by P. DEKKER (Comm. Delft II, pages 46—66), who proved that part of the nitrogen passes into the water—and the acetone-extract, while on the other hand only 60 % of the nitrogen is found amongst the insolubles after boiling with kerosene (compare § 247).

The factor 6.25 was rejected by D. SPENCE, who supposes the nitrogen to be present in the form of glycoproteids (compare § 247) containing 10 % of nitrogen, and not 16 % as the real proteins.

This point was discussed from several sides ; see for instance the review by P. DEKKER, l.c.

About the constitution of the proteins in rubber, their components and decomposition products very little is as yet known.

An estimate of the amino-derivatives, that are supposed to be accelerators of vulcanisation, proved their amount to be very small, much below 0.01 % of the dry rubber.

H. P. STEVENS, J. S. Ch. I. 36 (1917), 368.

On the presence of proteins and a number of amino-acids in rubber see F. FRANK, *Rubb. Ind.* 1914, page 146; also G. Ztg. 29 (1914), 196.

As to changes in the protein-content of the rubber in connection with the composition of the latex and the methods of preparation only the following data are available.

After opening a tapping cut the protein-content of the rubber gradually increases from day to day, whilst at the same time the total nitrogen in the latex decreases (compare § 29). The same changes are caused by heavy tapping as compared with mild tapping (§ 32). In these cases a higher nitrogen-content of rubber runs parallel with a greater rate of cure.

The method of coagulation may have an influence; some coagulants precipitate part of the proteins that others leave in the serum.

CL. BEADLE and H. P. STEVENS (VIII. Int. Congr. 9, page 17; Z. Koll. 13 (1913), 208) found the average protein-content in 20 samples of acetic acid coagulated crepe to be 3.04 %; in a latex, preserved with formalin, the naturally formed lumps contained 3.06 % of protein, whilst coagulation with alcohol gave a clot with 4.28 %, and evaporating the latex to dryness gave 8.48 % protein.

That the method of preparation, especially the degree of maturation, may have an influence on the nitrogen-content of the rubber is evident from § 108; the nitrogen-content in matured rubber may decrease to 0.15 %. On the other hand rubber obtained by total evaporation of the latex contains more nitrogenous substances and the nitrogen-content may be 0.5 % or more.

See B. J. EATON and F. W. F. DAY, Agric. Bull. F.M.S. 4 (1916), 352; J. S. Ch. I. 35 (1916), 726; Bull. F.M.S. 27 (1918), 97 and 105; further H. P. STEVENS, J. S. Ch. I. 36 (1917), 366.

The influence of the nitrogen derivatives on vulcanisation and especially on the rate of cure may be assumed as very important. We already mentioned (see § 108) that the action of protein decomposition products, formed by maturation, as accelerators of vulcanisation may be regarded as proved, though positive data as to which substances (chemically speaking) play a role, in what quantities they work, and in what quantities they are present in air-dry rubber, still absolutely fail.

* A. VAN ROSSEM (Comm. Delft VI, page 199) found that no correlation exists between the nitrogen-content of raw rubber and its rate of cure.

In § 112 we have already mentioned that the proteins obtained from serum by heating or on standing have no accelerating effect when added to ordinary plantation-rubber. The same is the case with other foreign proteins, such as

peptone and casein. Decomposed casein, dependent upon the way it was decomposed, contains an accelerator and may more or less increase the rate of cure.

B. J. EATON and J. GRANTHAM, J. S. Ch. I. 35 (1916), 722;
Bull. F. M. S. No. 27 (1918), 84. H. P. STEVENS, J. S. Ch. I.
36 (1917), 365.

When the rubber is freed of the greater part of the nitrogen derivatives (for instance by dissolving in benzene, filtering and recovering), it vulcanises very slowly. The addition to such a rubber of undecomposed protein has an accelerating action; the nitrogen-containing part, that was insoluble in benzene, or the proteins obtained by heat-coagulation of serum, markedly accelerate vulcanisation in such a rubber, as well as foreign proteins such as peptone or, to a lesser degree, casein; even a nitrogen-free substance such as starch may to a certain degree promote vulcanisation in such rubber. That ordinary, undecomposed proteins do not accelerate vulcanisation in ordinary plantation-rubber, would therefore have to be explained by assuming that such rubber already contains enough proteins.

See CL. BEADLE and H. P. STEVENS, J. S. Ch. I. 31 (1912), 1099; I. R. J. 44 (1912), 554 and 603; also Z. Koll. 11 (1912), 61. Further H. P. STEVENS, I. R. J. 47 (1914), 403; also Z. Koll. 14 (1914), 91.

§ 247. Insoluble constituents.

When rubber is dissolved in organic solvents, an insoluble part remains, which may vary considerably in amount and in constitution. It may contain part of the rubber-hydrocarbon, a large proportion of the nitrogenous matter, further some or the whole of the mineral substances, and other components of unknown nature and composition.

Dependent upon the solvent and the method and temperature of the extraction, the content of insolubles may vary between wide limits; figures between 0.4 and 25 % have been found in the same sample by different methods of extraction. Though a large amount of work on this group of constituents has already been done, our

knowledge is still very vague; exact, well defined data as to details, such as the separate components of the „insoluble part” in different methods of extraction, still fail.

Most of the older literature on this subject is reviewed in papers by CL. BEADLE and H. P. STEVENS (I. R. J. 44. (1912), 554 and 603; also Z. Koll. 11 (1912), 61) and D. SPENCE and G. D. KRATZ (Z. Koll. 14 (1914), 262). The latter authors showed that heating in benzene that contains 0.3 to 0.5 % of trichlor-acetic acid gives an excellent separation of the insolubles, the whole of the rubber dissolving easily. In the insolubles so obtained they found 9—12 % of nitrogen, and obtained reactions for proteins and carbohydrates, so that the nitrogen seems to be present in the form of a glycoprotein.

See further W. SCHMITZ (G. Ztg. 27 (1913), 1085 and 28 (1914), 1740) on the nitrogen-content of the insoluble part after different treatment.

P. DEKKER (Comm. Delft II, page 56) made a comparison between the insoluble parts left after extraction with different solvents. He especially recommends boiling with kerosene of a boiling point of 230—260° C which dissolves all the caoutchouc and leaves all the mineral matter and 55 to 65 % of the nitrogenous matter in the rest.

We will not go deeper into a discussion of the insoluble constituents of rubber, as the composition of the insolubles is still so vague and varying and as so little is known about their relation to the methods of preparation and the properties of the rubber.

About eventual changes in these constituents, dependent on the composition of the latex, no data are available.

Kneading and mechanical working have the effect that the insoluble part diminishes; whether this is caused by the proteins becoming more finely divided, is not yet certain.

CL. BEADLE and H. P. STEVENS, I. R. J. 44 (1912), 554; also Z. Koll. 11 (1912), 62.

That the insoluble part in a certain rubber is not a constant, is further proved by the fact that it increases, for instance, by heating the rubber at 130° C in the air or in carbon dioxide.

P. DEKKER, Comm. Delft II, page 63.

An explanation of such phenomena, and even the exact knowledge which constituents of the „insoluble part” undergo a change in such cases, still fail us, and will perhaps not easily be gained, judging from the complex colloidal nature of the substances in question.

When rubber is freed from the insoluble part—by dissolving in benzene at room temperature, filtering, and recovering by evaporation—it vulcanises slowly, whilst samples with an increased proportion of the insolubles show an increased rate of cure. The part that is insoluble in benzene at ordinary room temperature, and that contains a large proportion of nitrogenous substances, therefore contains an accelerator.

CL. BEADLE and H. P. STEVENS, I. R. J. 44 (1912), 554; also Z. Koll. 11 (1912), 63; *ibid.* 12 (1913), 47; J. S. Ch. I. 31 (1912), 1099; Z. Koll. 14 (1914), 91.

§ 248. Other components.

Quebrachite.

Of the water-soluble components of latex and serum nearly half is formed by quebrachite, which on account of its great solubility remains for the greater part in the serum (description and figures see § 7 and 111).

Whether quebrachite is generally present in ordinary smoked sheet and crepe, and to what amount, is not yet known. In rubbers prepared by evaporation or by other methods in which a large part of the serum-substances is retained, a larger content of water-soluble substances, and amongst them quebrachite, is to be expected; figures as large as 2.7 % quebrachite (calculated on the dry rubber) are mentioned for such rubber.

S. S. PICKLES and B. W. WHITFIELD (Proc. Chem. Soc. 27 (1911), 54) state that they have isolated quebrachite from „smoked plantation-rubber from the Malay Peninsula”, the substance being present in all cases, but the amount varying considerably, and being in some cases as high as 25 %. They found its occurrence quite general in rubber from *Hevea brasiliensis* and in Fine Hard Para. The presence of an appreciable quantity of a substance soluble in water, retained

in spite of the washing process, may be called unexpected in ordinary smoked sheet and especially in the thoroughly washed crepe (compare D. F. TWISS, J. S. Ch. I. 38 (1919), 49 T). From other publications (Agric. Bull. Str. F. M. S. 10 (1911), 145; Bull. Imp. Inst. 10 (1912), 25; Gard. Bull. 1 (1912), 151) it appears, however, that the high figures mentioned by PICKLES and WHITFIELD relate to smoked rubber prepared after the Brazilian method (and not to smoked sheets). By hot acetone 4.8 % (calc. on dry rubber) could be extracted from the balls, in which extract 2.7 % appeared to be quebrachite, and only the rest, 2.1 %, resins.

Although in our experiments (see Chapter XIV) with the Brazilian method of preparation approximately one half of the serum dripped from the balls during the first 24 hours, and a large part of the water-soluble quebrachite therefore will not have been incorporated in the rubber, it may well be that in the experiments in Singapore the evaporation was carried further, as the latex of only one tree was used, and the daily amount of latex therefore small. In fact, in the above named publication the presence of such a large amount of l-methyl inositol is explicitly explained by the circumstance that in this specimen of Para-rubber „the whole of the solid constituents of the latex remained in the rubber”. PICKLES and WHITFIELD proved the presence of this carbohydrate in Fine Hard Para rubber from South America but gave no figures for ordinary rubbers, prepared by acetic acid coagulation (smoked sheet or pale crepe).

The amount of quebrachite in latex undergoes only relatively small changes (see § 7 and 21); and as probably only a small part—if any — of this easily soluble substance is incorporated in the rubber in ordinary coagulation, the differences in the amount of quebrachite in ordinary rubber will not be of much importance.

As far as investigated, quebrachite has no influence on the vulcanising properties of the rubber. Whether it may serve as nutrition for moulds, or plays a role in the formation of rustiness, is not yet known.

H. P. STEVENS (J. S. Ch. I. 36 (1917), 367) found that addition of 3% of quebrachite to rubber freed from proteins by dissolving in benzene, retarded the rate of cure somewhat.

Enzymes.

Enzymes are present in the coagulum and the nearly dry rubber; an oxydising enzyme is responsible for the darkening

of the lower grades, and probably the change in tint of sheet-rubber during drying may be, at least partly, ascribed to some similar process. In dry market rubber enzymes have been also found; the data on this subject are, however, still scarce.

D. SPENCE (Biochem. Journ. 3 (1908), 168, also I. R. J. 35 (1908), 683 and 36 (1908), 25.

Other substances.

Amongst other substances occasionally found in rubber may be named formaldehyde, which may occur in smoked sheets and is evidently absorbed from the smoke.

See K. GORTER, Teysm. 22 (1911), 396.

CHAPTER XXII.

§ 249. Judging rubber from the exterior.

The external appearance of the rubber is the first thing that is completely abolished in manufacture, and no words need be wasted to prove that it is of no real importance in a raw material that never reaches the consumer in the form in which the market knows it. Still the thousands of tons of rubber that are handled in European and Eastern markets are judged exclusively — if at all — on the exterior. The hand, tooth and nail tests, formerly so much in vogue, have gradually lost in importance, as it is now well understood that a little pulling or pressing does not teach us much about what the rubber will be after such drastic treatments as vulcanisation or dissolving; but the standardisation of the market product according to its outward appearance remains the rule and the requirements have not become less, nor do they as yet show any tendency to reckon with what the manufacturer really wants or with what certain shortcomings really mean.

Judging rubber from the exterior appearance has, of course, in many cases a real importance which nobody will deny, especially when it is coupled with the large experience of the broker. Exclusively judging from the exterior, as is now the rule, can only be based on the conviction that the exterior teaches us in all cases whether the rubber was prepared with sufficient care, and that eventual shortcomings in preparation or properties very soon make themselves felt in the appearance. Now it is certainly true that many shortcomings and deviations from the best rules for preparation are visible; but amongst them there are a large number which are wholly without importance as regards the properties of rubber in manufacture. Such faults arouse an undue amount of suspicion (with the

accompanying reduction in price) while some of the principal points in a well-conducted standard preparation have no influence at all on the appearance and may have been badly neglected in rubber of the most attractive and uniform outward appearance.

We will illustrate this by some examples.

A standard dilution of the latex and standard methods of coagulating, milling and drying in general—which are of such vital importance to obtain a product of uniform vulcanising properties—result, to be sure, in a crop of more uniform appearance. The same may be said of mixing large quantities of latex. But this does not mean that estates which still follow the old, haphazard methods are recognizable on the market by a less uniform product: by a rather extensive sorting such estates grade their rubber according to a number of different colours, often differing only a little in shade, so that the chests may make a very uniform impression when opened for sampling. Nevertheless, the principal rules for securing uniform inner properties have been neglected, and the manufacturer is compelled to make a careful mixing and blending to ensure uniform lots. Estates following standard methods deliver a product of which chest after chest shows very nearly the same inner properties, as we have repeatedly shown in this book.

On the other hand very objectionable methods of preparation may give a rubber of good or even excellent appearance. We have mentioned (§ 88 and 105) that coagulation with a rather large dose of alum gives very elastic sheets with a strong feel; yet such sheets vulcanise abnormally slowly, much more slowly than is ever the case with ordinary plantation-rubber, whilst nothing in the exterior warns the buyer against this defect.

Factories which handle, wash, and crepe the rather large amount of stray rubber in the East, such as lots of every description from native holdings, remnants of plantation rubber, and the scrap of the Eastern industry in general, succeed remarkably well in working these very different

grades into a few types of rather thick crepe of uniform colour and appearance. Unless great care is taken in sorting before mixing the different grades, such crepes may show very variable vulcanising properties, because native rubber is prepared in so many different ways, from a fairly good procedure with acetic acid to the most reprehensible abuse of alum.

To give a still stronger though hypothetical example take the following. Suppose that during the scarcity of acetic acid in the beginning of the war estates had lacked the help and advice of institutes able to test the rubber, and had sought their own ways: the use of a coagulant such as the naturally acid water described in § 91 would have presented itself very readily. A crepe of good, rather pale appearance would have been obtained, which doubtless would have been welcome on the market; it would have been only after months that a tackiness would have begun to develop, which in a few years would have led to complete decay. Such rubber contains the germs of slow but sure deterioration, but nothing of it is visible on the exterior.

In these cases—to which many others might be added—rubber of good appearance, which fulfills all the demands of the market, may show mediocre or even very inferior inner properties. Many cases may also be mentioned in which rubber is rejected or depreciated because of faults in outward appearance which have nothing to do with properties of real importance and which only constitute insignificant unevennesses which are completely levelled up during the mixing and further operations in manufacture.

Faults such as an irregular pattern on sheets, for instance when the ribs on front and back do not coincide exactly, further folds or an uneven ridge at the edges or the end of the sheet, too many small holes in crepe etc.— faults which have nothing at all to do with the rubber itself — luckily do not attract the same amount of attention as in former years and are nowadays seldom heard of as giving rise to claims. Another quite innocent fault, viz. gas-bubbles or air-bubbles in the sheet — the inclusion of an indifferent

gas — are still regarded with some suspicion. Light cases pass the judges, but rather heavy cases are still rejected by those who, perhaps, would object still more strongly (if they knew) to the means by which these bubbles have to be prevented, viz. the use of more acetic acid in coagulation. They would, if they had the choice, quite unhesitatingly prefer coagulation „without the aid of acid” — that is spontaneous coagulation, in which in reality more acid is formed than one usually adds in the form of acetic acid, and which — striking example of the unreasonableness of such claims — gives a coagulum so porous that it cannot be worked into sheet because of . . . the numerous gas-bubbles.

Small traces of rustiness on sheet-rubber give rise to claims, though the decomposition of serum-substances on the surface of the wet sheet is quite innocuous and does not lead to more dangerous products than the decomposition that always takes place when the coagulum is kept overnight, and by which vulcanisation is slightly accelerated. Only in the case of rustiness the resultant small amount of a harmless, jelly-like substance dries up on the surface and becomes visible to the keen and suspicious eye of the rubber expert, while the decomposition products formed by similar causes in the interior of the coagulum or sheet remain invisible. Such decomposition passes unheeded, regardless of whether the micro-organisms were at work only a few hours, one night, or two or more days before their action was stopped by milling or drying. The invisible difference produced by natural accelerators, which may make itself felt in vulcanisation, is nothing to the market standard, while the almost unweighable amount of an indifferent substance such as slight rustiness on the outer surface — how insignificant compared with the loads of fillers that will later have to be incorporated into the rubber — bars the way to the title of „prime” or „standard” quality.

In preparing crepe-rubber sodium bisulphite has to be used to obtain an even and pale colour; otherwise a discolouration takes place on the surface of the coagulum

and the crepe becomes somewhat more brown and often streaky. This discolouration is caused by a very small amount of a strong colouring matter, produced not from the rubber itself, but from one of the serum-substances. An oxydation takes place, it is true, but it is not the rubber that is oxydised. Any influence from the colouring matter on the vulcanising properties of the rubber has thus far not been detected; and then, how little influence such a trace of a foreign substance can have, compared with the amounts of pigment that are added in the manufacture of many articles. The use of bisulphite does no harm, as was formerly supposed by some; but it augments somewhat the costs, and would seem superfluous in many cases.

Similar remarks also apply to many of the spots caused in crepe or sheet by micro-organisms: often a trace of a strong colouring matter is formed, which is very striking to the eye, but does no harm to the rubber. Though a claim is justified in such cases when the arrangement was to deliver rubber free from spots, the reduction in price would often seem wholly out of proportion to the real depreciation in quality. In contrast to such cases stand others in which a real deterioration of the rubber has indeed taken place. When an estate recrepes such rubber to get rid of the spots, the resulting perhaps somewhat darker crêpe, which is really inferior, is received on the market without objection.

The idea of testing all rubber as it comes to the market and of selling it on certificate of quality was very thoroughly gone into in 1913 and 1914; (see for instance *I. R. J.* 46 (1913), 757, 820, 1215 and 1264; 48 (1914), 75, 805 and 1047; 49 (1915), 254) but the amount of work and the cost of testing all rubber in a relatively short time were found to be too great. Still, something might certainly be done in a simpler form; for instance, guarantees or certificates might be issued by estates which strictly adhere to standard methods of preparation and have their product regularly tested and controlled in the way we have described in foregoing chapters. It would still have to be proved whether such a certificate-rubber could awaken an interest on the

market which — and that for sound reasons — changes its habits only slowly and after due deliberation.

Still, as most of the present prejudices are presumably caused by a lack of sound knowledge of the properties of rubber and of their real importance in preparation and manufacture, we hope that the spreading of such knowledge of rubber as is at present available—which is the principal aim of this book—may be of some benefit to the industry.

ABBREVIATIONS OF LITERATURE.

Agric. Bull. F.M.S.	Agricultural Bulletin of the Federated Malay States (Kuala Lumpur).
Agric. Bull. Str. F.M.S.	Agricultural Bulletin of the Straits and Federated Malay States, Singapore, 1902—1911.
Ann. Bot.	Annals of Botany (London).
Ann. J. Bot.	Annales du Jardin Botanique de Buitenzorg.
Ber.	Berichte der Deutschen Chemischen Gesellschaft (Berlin).
Biochem. Journ.	The Bio-Chemical Journal (Liverpool).
Brown, Rubber	Rubber, its sources, cultivation and preparation, by H. Brown; Imperial Institute series of Handbooks (London, John Murray, 1914).
Bull. Ass. Pl.	Bulletin de l'Association des Planteurs de Caoutchouc (Anvers).
Bull. Ceyl.	Bulletin of the Department of Agriculture, Ceylon (Colombo).
Bull. F.M.S.	Bulletin of the Department of Agriculture in the Federated Malay States (Kuala Lumpur).
Bull. I. Ch.	Bulletin Economique de l'Indochine (Hanoi-Haiphong).
Bull. Imp. Inst.	Bulletin of the Imperial Institute (London).
Bull. Mars.	Bulletin des Caoutchoucs de l'Institut Colonial de Marseille.
Bull. R.G.A.	Bulletin of the Rubber Growers' Association Inc. (London).
Bull. Saigon	Bulletin Agricole de l'Institut Scientifique de Saigon.

Bull. Sur.	Bulletin van het Departement van den Landbouw in Suriname (Paramaribo).
Ceyl. Adm. R.	Administration Reports, Department of Agriculture, Ceylon.
Ceyl. R. E. 1906	The Ceylon Rubber Exhibition, September 1906. Descriptive Account and full Reports (A. M. and J. Ferguson, Colombo).
C. Gp.	Le Caoutchouc et la Gutta Percha (Paris).
Circ. R. B. G.	Circulars and Agricultural Journal of the Royal Botanic Gardens, Ceylon (Colombo).
Comm. Delft	Communications of the Netherland Government Institute for advising the Rubber Trade and the Rubber Industry, established at Delft (Holland). Translated in English under the auspices of the International Association for Rubber Cultivation in the Netherland Indies (the Hague).
C. R.	Comptes Rendus de l'Académie des Sciences, Paris.
Gard. Bull.	The Gardens Bulletin, Straits Settlements (including the Agricultural Bulletin of the Straits and Fed. Malay States, third series), Singapore.
G. Ztg.	Gummi Zeitung (Berlin).
Ind. Rubb.	C. O. Weber, The Chemistry of India Rubber (London, 3 ^d Impr. 1909).
VIII Int. Congr.	Eighth International Congress of Applied Chemistry, New York 1912, Original Communications.
I. R. J.	India Rubber Journal (London).
I. R. W.	India Rubber World (New York).
J. d'A. T.	Journal d'Agriculture Tropicale (Paris).

J. S. Ch. I.	Journal of the Society of Chemical Industry, London.
Kautschuk	Der Kautschuk, eine Kolloidchemische Monographie, von Dr. R. Ditmar (Berlin, J. Springer, 1912).
K. & Pr.	Der Kautschuk und seine Prüfung, von F. W. Hinrichsen und K. Memmler (Leipzig, S. Hirzel, 1910).
Lectures 1908	Lectures on India Rubber, Official Account of the International Rubber and Allied Trades Exhibition London 1908, edited by D. Spence.
Le Latex	Le Latex, son utilisation directe dans l'Industrie, par le Dr. Lucien Morisse (Paris, A. Challamel, 1908).
Mal. T. & R. J.	Malayan Tin and Rubber Journal (Ipoh, F. M. S).
Mat. Pr.	Mitteilungen aus dem Königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Med. Pl.	Mededeelingen van 's Lands Plantentuin te Buitenzorg.
Med. Rubber	Mededeelingen over Rubber (issued in Dutch by the Department of Agriculture, Buitenzorg, Java).
Med. W. J.	Mededeelingen van het Rubberproefstation West-Java (Buitenzorg).
Phys. & Diseases	The Physiology and Diseases of Hevea brasiliensis, by T. Petch (London 1911).
Prep. Pl. Rubber	S. Morgan, The Preparation of Plantation Rubber (London, 1913).
Proc. Chem. Soc.	Proceedings of the Chemical Society, London.
Proc. III ^d Congr. 1914	Proceedings of the Third International Congress of Tropical Agriculture, London 1914 (London, John Bale Sons & Danielsson Ltd, 1914).

Rec.	Recueil des Travaux Chimiques des Pays Bas (Leyde).
Rubber	Rubber, by Ph. Schidrowitz (Methuen & Co, London, 1911).
Rubb. Ind. 1911	The Rubber Industry, Official Report of the International Rubber Congress London 1911, edited by J. Torrey and A. Staines Manders.
Rubb. Ind. 1914	The Rubber Industry, Official Report of the Fourth International Rubber Congress, London 1914, by J. Torrey and A. Staines Manders.
Rubb. Rec. 1914	International Rubber Congress and Exhibition, Batavia 1914, Rubber Recueil (De Bussy, Amsterdam).
Seeligm.	Th. Seeligmann, G. Lamy-Torrilhon & H. Falconnet, Le Caoutchouc et la Gutta Percha (Paris, J. Fritsch, 1896).
Teysm.	Teysmannia (edited in Dutch at Buitenzorg).
Trop. Life	Tropical Life (London).
Trop. Agric.	The Tropical Agriculturist (Colombo).
Tropenpfl.	Der Tropenpflanzer (Berlin).
Wright	Herbert Wright, Hevea Brasiliensis or Para Rubber, IV Edition (Maclaren & Sons, London, 1912).
Z. angew.	Zeitschrift für angewandte Chemie (Berlin—Leipzig).
Z. Bakt.	Zentralblatt für Bacteriologie, Parasitenkunde und Infektionskrankheiten (Jena).
Z. Koll.	Zeitschrift für Chemie und Industrie der Kolloide (Dresden und Leipzig).

In the case of papers which have appeared in the same form in several Journals, two or more of them are generally quoted for the use of readers who have not all the above literature at their disposal. This is indicated in the quotations by the word „also”.

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CORRIGENDA.

Estate Rubber, its Preparation, Properties and Testing, by Dr. O. de Vries.

To the „CORRIGENDA” on page 649 add :

page 15, line 23 from above read give instead of gives

„ 67,	„ 8	„	„	„ procedure	„	„ procedur
„ 303,	„ 5	„	„	„ 170	„	„ 171
„ 345,	„ 28	„	„	„ penny	„	„ ct
„ 470,	„ 10	„	„	„ estate	„	„ estates

„ 634, add: Arch. Archief voor de Rubbercultuur in
Ned. Indië (Buitenzorg).

